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Treating Wood Preserving Plant Wastewater by Chemical and Biological Methods

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TREATING WOOD PRESERVING PLANT WASTEWATER BY CHEMICAL AND BIOLOGICAL METHODS

by

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

"Treating Wood Preserving Plant Wastewater By Chemical And Biological Methods" was a part of the Industrial Pollution Control Division's program to develop and demonstrate new technology for the treatment of industrial wastes. This project demonstrated the biological treatment of wood preserving wastes containing pentachloropenols and creosote using complete mixed activated sludge. The study showed that the system could obtain BOD removals of 90 percent and phenol removals of 99 percent. The information will be of value to consultants and industry concerned with installation of treatment facilities to meet more rigid effluent standards. For further information, please contact the Food and Wood Products Branch of the Industrial Environmental Research Laboratory, Cincinnati.

David G. Stephan
Director
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Cincinnati

ABSTRACT

A completely mixed activated sludge system was designed for a wood preserving plant with an average daily wastewater flow of 27,000 /day (7,150 gal/day), a BOD concentration of 1,100 mg/l, and a phenol concentration of 120 mg/l. Included in the design were capabilities for pre-chlorination and post-chlorination. The activated sludge system lone was capable of removing 90 percent BOD, 75 percent COD, 99 percent phenol, and 76 percent pentachlorophenol. Shock loadings had minor effects on BOD and COD removals but reduced the phenol removal and completely prevented pentachlorophenol removal.

Post-chlorination dosages of over 50 mg/l resulted in reductions of 50 and 52 percent for phenol and pentachlorophenol, respectively, during the study. The Safranin method was used for measuring penta. Later follow-up work by Koppers using vapor phase chromatography with electron detection showed penta reductions of 5 mg/l to 0.1 mg/l. There was no reduction of COD. A pre-chlorination study showed no removal of phenol, pentachlorophenol, or COD at the level studies in the full scale plant. Laboratory pre-chlorination studies showed removal of phenol and pentachlorophenol at chlorine dosages in excess of 250 mg/l.

This report was submitted in fulfillment of EPA Grant No. 12100 HIG by Environmental Science and Engineering, Inc., Gainesville, Florida, for Koppers Company, Inc., Pittsburgh, Pennsylvania, under partial sponsorship of the Water Quality Office, Environmental Protection Agency. The study was completed as of July 1974.

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Environmental Science and Engineering, Inc., (ESE) of Gainesville, Florida, as a consultant to Koppers Company, provided overall supervision of the project. The concepts of the program and the treatment facilities were developed by Dr. Richard H. Jones, P.E. The Project Manager for the first year of the project, Mr. T. A. Bursztynsky, P.E., was responsible for planning the technical program. Mr. John T. White supervised much of the program and contributed substantially to preparation of this report. Mr. John D. Crane, P.E., supervised preparation of the final report and coordinated reviews by EPA and Koppers personnel. Dr. W. S. Thompson of the Forest Products Research Laboratory, Mississippi State University, provided valuable consulting services to ESE.

KOPPERS COMPANY

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ENVIRONMENTAL PROTECTION AGENCY

The Project Officer was Mr. Victor Dallons. Technical review and assistance were provided by Mr. Ralph Scott and Mr. James H. Phillips. The program was partially funded by EPA under Grant No. 12100 HIG.

SECTION I

CONCLUSIONS

It was demonstrated that wastewater from a wood preserving process utilizing creosote and pentachlorophenol (penta) as preservatives can be effectively treated by a biological system. The process employed was the complete mix activated sludge process. The process obtained a BOD reduction of 90 percent and a phenol removal efficiency of 99 percent.

Pre-chlorination was effective in reducing both penta and phenol in laboratory tests. However, in the full scale plant, a chlorine/penta ratio of 300:1 was required to achieve an 80 percent reduction in penta and the resulting excessive chlorine residuals caused operational problems in the biological treatment system.

Post-chlorination provided considerable color removal and reduced the penta concentration from about 5 mg/l to less than 0.10 mg/l. It also accomplished slight reductions in phenol concentrations. There was no apparent reduction of COD.

Shock loading tests showed a noticeable decrease in treatment efficiency. A doubling of the hydraulic loading rate resulted in a decrease in phenol removal from 99 to 89 percent, in COD from 80 to 72 percent, and penta from 79 to 0 percent. There was little apparent effect on BOD removal efficiency.

The usefulness of BOD as a pollutant parameter was limited as the characteristics of the wastewater apparently inhibited the test, e.g., an increase in dilution in the BOD test from 99.8 to 99.9 percent resulted in an increase in BOD from 1000 to 2000 mg/l.

The Safranin method for measuring pentachlorophenol was of questionable reliability in testing the biological treatment effluent; an increase in penta was indicated across the activated sludge unit. It should be noted that near the end of the study, vapor phase chromatography using electron capture detection was found to be a relative method for penta detection at low levels and indicated that the Safranin analyses were generally high.

SECTION II

RECOMMENDATIONS

The activated sludge process provides a potential means as a viable treatment alternative for the treatment of wood preserving wastewater where limited land is available for spray irrigation and lagooning. For plants which have limited land available for spray irrigation or lagooning, the activated sludge process could represent the most cost-effective treatment alternative. The activated sludge process should be recommended to the wood preserving industry as a potential means of meeting increasingly stringent effluent limitation standards.

A properly designed and operated preservative recovery system is recommended before activated sludge treatment. Also, a surge basin is imperative for successful operation of the activated sludge system.

The key design parameters for the complete mix system are as follows:

1. Maximum BOD Loading = 0.2 kg/day/kg MLSS
2. Maximum COD Loading = 0.5 kg/day/kg MLSS
3. Maximum Penta Loading = 6.5 gm/day cu m
4. Minimum hydraulic detention time = 40 hours

SECTION III

INTRODUCTION

The Koppers Company, Inc., wood preserving plant at Carbondale, Illinois, was selected by the Environmental Protection Agency in 1971 as a site for a demonstration project to determine the design and operating parameters for chemical and biological treatment of both creosote and pentachlorophenol (penta) wastewaters generated by a wood preserving operation. The wastewater from the Carbondale plant is representative of wood preserving wastewater in that it has a high Biochemical Oxygen Demand (BOD) and contains wood preserving compounds and extractives. The successful development and operation of treatment facilities at the Carbondale plant alleviates a specific pollution problem at that plant and, more importantly, provides design parameters for similar wood preserving plants.

BACKGROUND

A number of methods have been developed to increase the serviceability of wood under conditions that promote decay, weathering, insect destruction, or exposure to fire. Treated or preserved wood is used in almost every facet of the construction industry. Included among the various wood materials that are treated with preservatives or fire retardants are general lumber and timber, bridge ties, foundation piles, posts, crossties, utility poles, and marine construction wood.

Preservative and Fire Retardant Chemicals

The various preservatives in common use throughout the industry include creosote, creosote-coal tar, creosote-petroleum and pentachlorophenol solutions, as well as water-borne preservatives and fire retardants. Creosote, creosote-coal tar, and pentachlorophenol-oil preservatives are used at the Koppers Company facility at Carbondale; however, creosote is the principal preservative used.

Creosote, a distillate of tar produced by the carbonization of bituminous coal, is used as a wood preservative both because it protects wood against wood destroying organisms and has a high degree of perseverance. The main constituents of creosote are tar acids.

The mixture of creosote with coal tar is primarily for railroad ties and marine installations that require a preservative with water-repelling properties. Common ratios of creosote to coal tar are 80:20, 70:30, 60:40, and 50:50.

Pentachlorophenol, frequently called "Penta", has a relatively low solubility in water of about 15 mg/l at normal water temperatures. It is normally applied with a carrier petroleum oil.

Water-borne preservatives are basically heavy metal compounds of copper, chromate, arsenite or arsenate, and zinc. One of the chief advantages of this treatment is that the wood is paintable. Water-borne preservatives are not used at the Carbondale plant.

Fire retardant formulations are designed to slow the spread of fire in treated wood. There are generally four formulations used in the industry, with water used as the preservative carrier. Prior to the commencement of the investigation, the Carbondale Facility used a formulation containing a borate.

Description of the Wood Preserving Process

The wood preserving process consists of two basic steps: (1) preconditioning the wood to reduce its natural moisture content and (2) impregnating it with the desired preservatives. The moisture reduction step may consist of (1) seasoning or drying the wood in large, open yards, (2) kiln drying, or (3) steaming the wood for several hours at elevated pressures to raise the temperature of the moisture in the wood cells, and subsequently applying a vacuum to reduce the boiling point of the water and evaporate it. Nearly 70 percent of the wood produced at the Carbondale plant consists of crossties and switch ties which are air seasoned in a storage yard. Approximately 10 percent of the production at the Carbondale plant is pretreated by steaming. Kiln drying requires from four to ten days for pretreatment as compared to approximately 12 hours for steaming.

Pretreatment of wood by steaming may be done in one of three ways: (1) open steaming, (2) closed steaming, and (3) semi-closed steaming. Open steaming consists of placing the wood in retorts and applying steam under pressure to the retorts for a period of several hours after which vacuum is applied to remove wood water to the effluent system. As the applied steam condenses on the wood and on the sides of the retort, it drains down and is eventually removed as wastewater. This condensate tends to collect preservatives deposited in the retort from previous processing.

In the closed teaming cycle, water is introduced into the retort and the wood is heated by steam generated by heating coils in the bottom of the retort. At the end of the cycle , the water is withdrawn to a storage tank from which it may be reused. Eventually a blowdown of the steaming water is necessary because of the buildup of wood extractives. At Carbondale this blowdown goes to the treatment system.

The Carbondale plant uses four retorts for the application of the semi-closed steaming cycle for wood pretreatment. In this process, steam is added to the retort under vacuum to reduce the condensation temperature and lower the boiling temperature of water entrained in the wood. As steam condenses in the retort, the liquid level is allowed to build up until it covers the heating coils in the bottom of the retort. Live steam is then turned off and heat is applied to the coil. At the end of steaming all water is discharged to waste and a vacuum continues to be drawn to remove additional moisture from the wood.

After the initial pretreatment step, there are several possible ways to impregnate wood with preservatives. For all creosote and pentachlorophenol treatments not requiring a heavy saturation of preservatives, the Carbondale plant uses the empty-cell Rueping process. The full-cell process is used for treatment applications requiring heavy saturations and for applications of fire retardant.

The empty-cell Rueping process provides greater penetration of preservative for net amounts of preservative absorbed and allows a relatively high recovery of excess preservative. The full-cell process allows a higher saturation of preservative within the wood cells.

Wastewater Sources from the Wood Preserving Process

The basic wood preserving process generates wastewater streams consisting of condensed water from steaming, barometric leg cooling water or surface condenser condensate, boiler blowdown, miscellaneous wash water, pipe and tank leakages, and door pit drips.

In the semi-closed steaming process, by which condensate is allowed to accumulate in the retort until it covers the heating coils, the condensate is wasted after oil recovery. The wasted condensates contain oil, phenolic compounds, and various wood extractives.

When barometric legs or wet-type vacuum pumps are used to produce vacuum, a water contaminated with the preservative used is generated. The Carbondale facility employs a vacuum pump preceded by a surface condenser. Volatile gases are condensed on the surface condenser and are discharged to waste. The pump is sealed and lubricated by water circulated through a small pond.

Boiler blowdown is usually a stream of small volume, but one that can be contaminated with various chemicals such as chromates and phosphates used for boiler water conditioning.

Water used to clean equipment is normally contaminated with preservative chemicals, oil and grease, and possibly detergents.

Existing Wastewater Treatment Facilities at Initiation of Project

The wastewater treatment system in employment at the Carbondale plant at the time of project initiation is illustrated in Figure 1. Since specific preservatives are used in a retort, it is possible to segregate wastewaters for pretreatment. Wastewater from the pentachlorophenol oil retorts is pumped to a decanter from which the floating oil fraction containing pentachlorophenol is recovered. The water fraction, after addition of a polymeric flocculant, is pumped

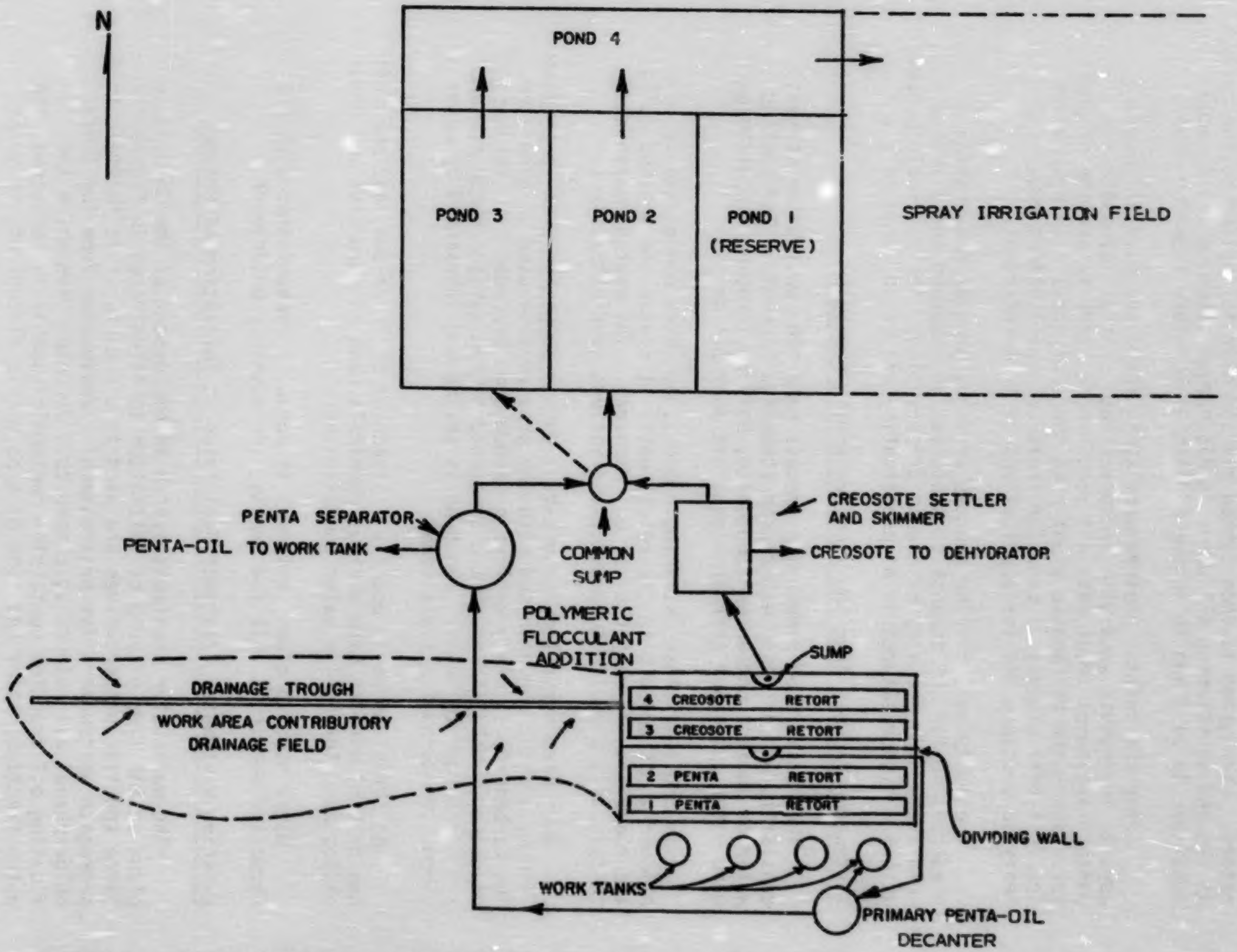
N
POND 4
POND 3
POND 2
POND 1
(RESERVE)
SPRAY IRRIGATION FIELD
PENTA SEPARATOR
PENTA-OIL TO WORK TANK
COMMON SUMP
CREOSOTE SETTLER AND SKIMMER
CREOSOTE TO DEHYDRATOR
POLYMERIC FLOCCULANT ADDITION
SUMP
DRAINAGE TROUGH
WORK AREA CONTRIBUTORY DRAINAGE FIELD
4 CREOSOTE RETORT
3 CREOSOTE RETORT
2 PENTA RETORT
1 PENTA RETORT
DIVIDING WALL
WORK TANKS
PRIMARY PENTA-OIL DECANTER

FIGURE 1. Original Wastewater Treatment Flow Diagram - Koppers Company, Carbondale

to a secondary recovery tank for further separation. The water from the second tank is transferred to a common sump.

Wastewaters are collected and handled separately in a similar manner as the penta-oil wastewaters with recovered creosote returned to the system. The clarified water is discharged to the common wet well.

The wastewater from the common sump is pumped to the set of four lagoons which provides equalization, evaporation, and biological oxidation. A spray irrigation field provides final treatment.

PROJECT OBJECTIVES

The project objectives were to determine the design and operating parameters of chemical and biological treatment of creosote and pentachlorophenol-oil wastewaters from a wood preserving plant. The plan of operation consisted of design, construction, and operation of treatment facilities for the wastewaters generated by the Koppers Company wood preserving plant located at Carbondale, Illinois. The operation and sampling and testing program would be supervised by Environmental Science and Engineering, Inc., of Gainesville, Florida.

SECTION IV

LITERATURE REVIEW AND PRELIMINARY STUDIES

In order to best meet the objectives of the project, an extensive review of the literature and other previous work related to the treatment of wood preserving wastes was conducted.

PHYSICAL TREATMENT

The first step in treating wastewater from a plant using creosote or creosote solutions is usually settling and skimming, not so much for treating wastewater, but to recover valuable preservatives. The most common type of separator in use by the industry is modeled after the separator developed by the American Petroleum Institute (1) which basically consists of a horizontal tank divided into three or more compartments. Heavy oils settle to the bottom of the tank and are removed by a pump to a dehydrator. Floating oils are removed by a skimmer.

The amount of entrained oils removed by separation equipment depends in part on whether the oil is in a free or emulsified form. Data on the percent efficiencies of several separators are presented in Table 1 (2). The variability of oil removal as a function of detention time was shown by Wallace, et. al. (3), as illustrated in Figure 2.

TABLE 1. EFFICIENCIES OF OIL SEPARATION PROCESSES

	Source of Influent	Percent Removal	
		Free Oils	Emulsified Oils
API Separator	Raw Waste	60 - 99	Not applicable
Air Flotation without Chemicals	API Effluent	70 - 95	10 - 40
Air Flotation with Chemicals	API Effluent	75 - 95	50 - 90
Chemical Coagulation and Sedimentation	API Effluent	60 - 95	50 - 90

The conventional oil-water separators discussed above remove only free oils. Emulsions may be broken by rotary vacuum filters or by centrifugation. Both of these methods have been tested at a few wood preserving plants, but chemical methods involving flocculation and sedimentation are the most widely used.

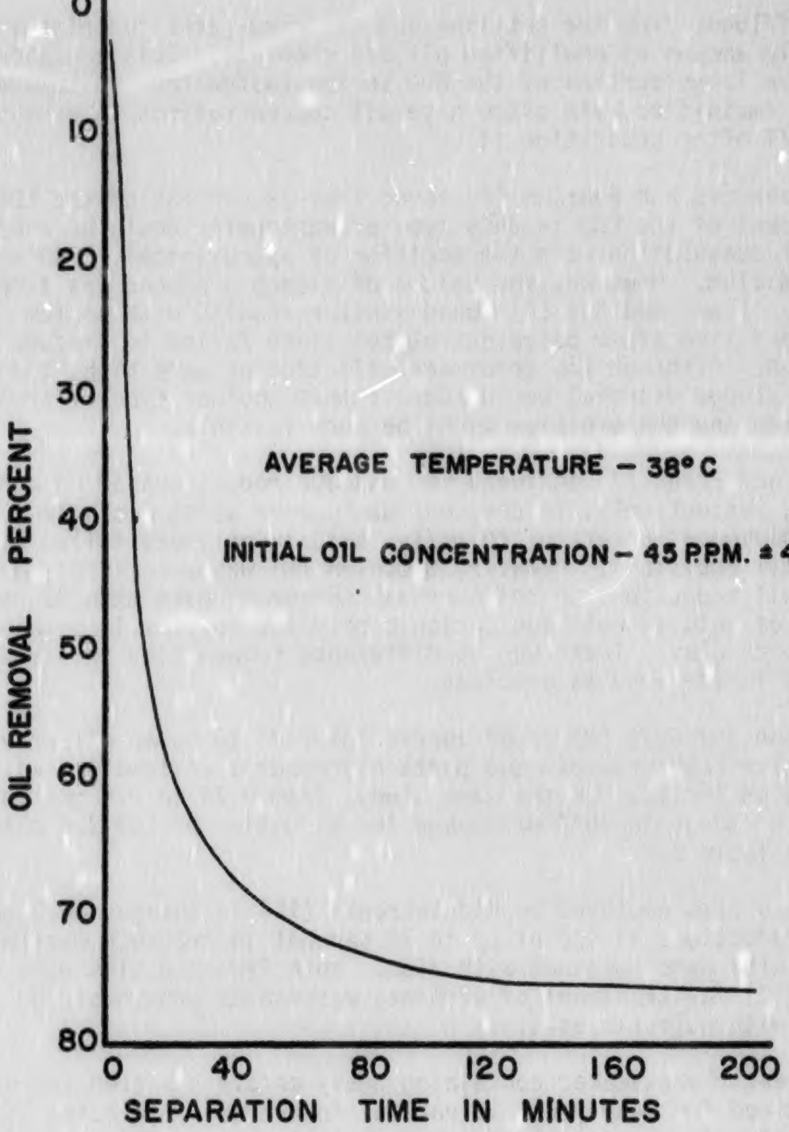

FIGURE 2
Effect of Detention Time on Oil Removal by Gravity Separation

CHEMICAL TREATMENT

Chemical Precipitation

The effluent from the settling and skimming tanks contains a considerable amount of emulsified oil and creosote. This emulsion represents a large portion of the BOD in the wastewater; wastewaters containing emulsified oils often have oil concentrations in excess of 1000 mg/l after separation (4).

Middlebrooks and Pearson (5) found that 79 percent of the BOD and 80 percent of the COD in this type of wastewater could be removed by chemical coagulation with the addition of approximately 2000 mg/l of lime and alum. However, the volume of sludge produced was almost 40 percent. Frank and Eck (6) found similar results with sodium hydroxide and lime after polyelectrolytes alone failed to produce flocculation. Although the treatment efficiencies were high, the problem of sludge disposal would suggest that another type of treatment for breaking the emulsion might be more feasible.

Jones and Frank (7) achieved COD and BOD reductions of 83 and 73 percent, respectively, in creosote wastewater using a single cationic polymer at a rate of 40 mg/l. Anionic polymers failed to break the oil emulsions. However, Simonsen (8) was successful in obtaining oil reductions in refinery wastewater of more than 95 percent by the use of both anionic and cationic polyelectrolytes in combination with bentonite clay. There was no difference between the two types of polymers in the results obtained.

Thompson and Dust (9) found ferric chloride to be an effective flocculant for both creosote and pentachlorophenol wastewaters with very narrow pH limits. In the same study, from 0.75 to 2.0 gm/l of lime appeared to be an optimum dosage for reduction of COD and phenol, as shown in Table 2.

Lime was also employed by Middlebrooks (10) in dosages of 2 gm/l to obtain reductions in COD of up to 70 percent in creosote wastewater. Similar results were obtained with alum. Both lime and alum were used by Gaspin (11) for treatment of creosote wastewater previously de-emulsified with sulfuric acid.

Treatment of wastewater containing heavy metals has been successfully practiced for many years in various industries. Chromium is found in wastes from metal plating and finishing operations. It is present in rinse waters and chromic acid baths and in spent baths from electroplating and anodizing processes. Wastewaters from similar processes also contain copper and zinc.

Heavy metals contained in salt-type preservatives and fire retardants are toxic to microorganisms, even when the metals are in relatively low concentrations (12) (see Table 3). Other studies (13), using a combination of metals, showed that the aeration phase of biological treatment can tolerate chromium, copper, nickel, and zinc, up

TABLE 2. EFFECT OF LIME FLOCCULATION ON COD AND PHENOL CONTENT OF TREATING-PLANT EFFLUENT

Lime (gm/l)	pH	COD Conc. (mg/l)	COD Percent Removal	Phenol (mg/l)
0.0	5.3	11,800	--	83
0.25	6.8	9,700	23	81
0.50	7.9	7,060	39	72
0.75	9.7	5,230	56	78
1.00	10.5	5,270	55	80
1.25	11.4	5,210	56	84
1.50	11.8	5,210	56	83

TABLE 3. THRESHOLD TOXIC LEVELS FOR CONTINUOUS DOSAGES IN AEROBIC TREATMENT PROCESSES

Metal	Wastewater Concentration (mg/l)
Chromium (VI)	10
Copper	1
Nickel	1-2.5
Zinc	5-10

to a total heavy metal concentration of 10 mg/l, either alone or in combination, with about 5 percent reduction in overall plant efficiency. Various other studies (14, 15, 16), both in the laboratory and in the field, reached similar conclusions.

Chemical analyses to determine heavy metal concentrations should be conducted on the wastewater from wood preserving plants using water-borne preservatives. If heavy metal removal is necessary, chemical treatment related to the specific ions present is applied. Usually precipitation of heavy metals from wastewater is accomplished with lime; however, hexavalent chromium must be reduced to a trivalent state by ferrous sulfate or sulfur dioxide prior to lime precipitation. The use of sulfur dioxide has been described in detail by Chamberlin and Day (17) and Fisher (68).

A bibliography dealing with the removal of heavy metals was compiled in 1949 by Dodge and Reamms (18) and it has been estimated by the American Wood Preserver's Association (19) that by 1959 some 500 additional articles had been published on the subject. Detailed discussions of heavy metal removal have also been presented by Eckenfelder (20) and Bliss (21).

Chemical Oxidation

While some information is available on oxidation of phenols using peroxide, ozone, and other chemical oxidants (22, 23), the vast majority of literature is concerned with the oxidation of phenolics with chlorine especially as related to the water supply area. It has long been common knowledge that chlorination of phenols may produce tastes and odors in water supplies. Early studies on chlorination of phenols centered on chlorine residuals and removal of tastes from water. Based on ratios of chlorine to phenol, Ingols and Ridenour (24) concluded that a quinone-like substance was the basic cause of "phenol" tastes. Their work postulated a succession of chlorination products which ultimately ended in dichlor-quinone. Further chlorination of dichlor-quinone was postulated to rupture the benzene ring and form maleic acid rather than completely eliminate any residual taste problems.

Subsequent studies by Ettinger and Ruchhoft (25) substantiated early work showing increasing taste intensity with increasing chlorination of phenols and then decreasing taste until no taste was noticeable and a chlorine residual began to develop. Comparative information was provided on the chlorination of various phenolic compounds and quantities of chlorine needed to eliminate detectable taste products. Table 4 indicates that a chlorine to cresol ratio of 5:1 would be adequate to completely form chlorination end products. Pentachlorophenol could be oxidized by chlorine at a 1:1 ratio.

The first fact substantiated from early work of researchers was the progression of chlorination products as illustrated in Figure 3. In more recent studies, R. G. Burttschell and co-researchers (26) at the Robert A. Taft Sanitary Engineering Center uses paper chromatography and infrared and ultraviolet spectrophotometry to determine the actual products

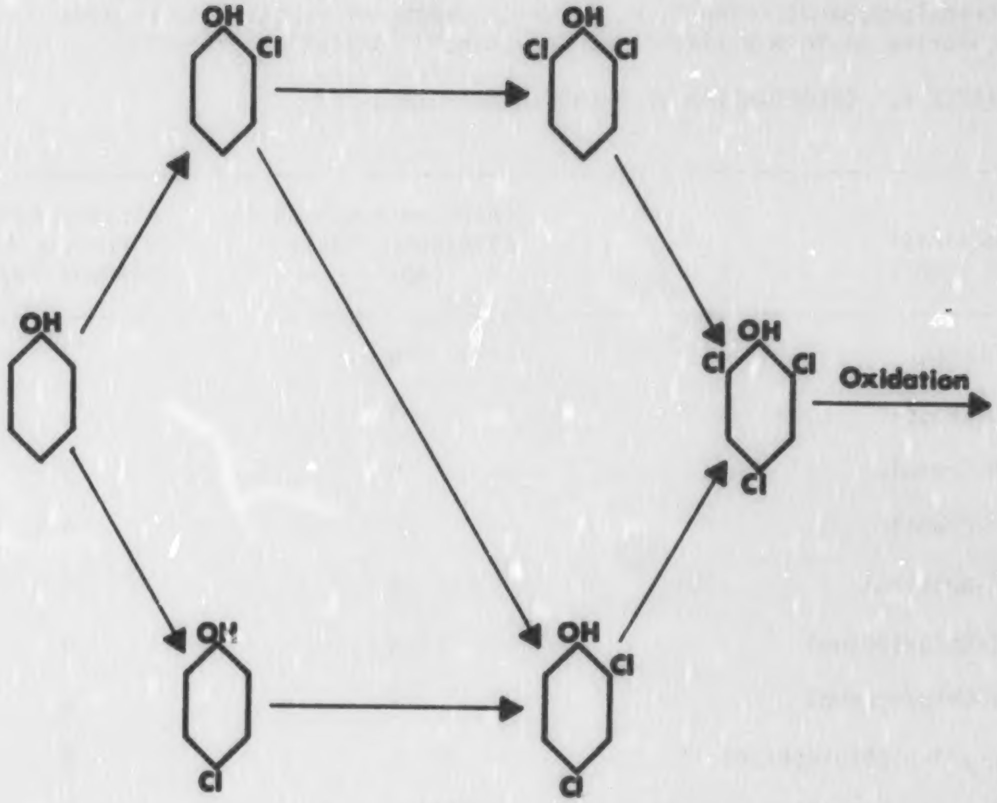
OH
Cl
Oxidation

FIGURE 3. Reaction Scheme for the Chlorination of Phenol

involved in the chlorination of phenols. According to these studies, the chlorination of phenol proceeds by stepwise substitution of the 2, 4, and 6 positions of the aromatic ring. Initially, phenol is chlorinated to form either 2- or 4- chlorophenol. Then 2- chlorophenol is chlorinated to form either 2, 4- dichlorophenol or 2, 6- dichlorophenol while 4- chlorophenol forms 2, 4- dichlorophenol. Both 2, 4- and 2, 6- dichlorophenol are chlorinated to form 2, 4, 6- trichlorophenol. The 2, 4, 6- trichlorophenol reacts with aqueous chlorine to form a mixture of non-phenolic oxidation products.

TABLE 4. CHLORINATION OF PHENOLIC MATERIALS

Material @ 1 mg/l	Chlorine Required to Eliminate Taste (mg/l)	Chlorine Added to Produce Free Residual (mg/l)
Phenol	4	7
O-Cresol	5	5
M-Cresol	5	5
P-Cresol	3	4
1-Naphthol	4	5
2-Chlorophenol	3	5
4-Chlorophenol	3	6
2-, 4-Dichlorophenol	2	6
2-, 4-, 6-Trichlorophenol	Could Not be Tasted	3
2-, 4-, 5-Trichlorophenol	Could Not be Tasted	2
2-, 3-, 4-, 6-Tetrachlorophenol	Could Not be Tasted	1.5
Pentachlorophenol	Could Not be Tasted	1.0

The principal taste causing compounds were found to be 2- chlorophenol, 2, 4- dichlorophenol, and 2, 6- dichlorophenol. The development of the chlorophenolic taste did not occur at pH values less than 7.0 and the presence of ammonia significantly retarded the rate of reaction between phenol and chlorine. Of prime importance was the discovery that at a chlorine to phenol ratio of 10:1, the aromatic benzene ring is destroyed. An optimum pH of 8 was found to be helpful for rapid chlorination of phenolic compounds using hypochlorous acid; however, reaction rates would be different under acidic conditions using chlorine gas since molecular chlorine is the most probable reacting agent. Therefore no information was provided on the mechanism of chlorination or reaction rates using chlorine gas at low pH values.

Later studies by Lee (27) provided information on the kinetics of reaction of phenolic compounds and chlorine. According to Lee, the chlorination of phenol and each of the chlorophenols conforms to a second-order rate expression in which the rate of change of chlorine or phenolic compounds is proportional to the product of the formal concentrations of aqueous chlorine and phenolic compounds, or:

$$\frac{-dF_{Cl}}{dt} = K_{ob} \; F_{Cl} \; F_{PhOH}$$

Rate constants were determined for each phenol compound at various pH levels and are plotted in Figure 4.

Obviously, the rates of reaction of aqueous chlorine with phenol vary with pH with the maximum rate of reaction occurring near neutrality for most species. It should be noted that the more acidic the phenolic compound the lower the pH of maximum reaction rate, and, as stated by Lee, those substitute groups of phenol which tend to make the substituted phenol more acidic also tend to decrease the rate of reaction of aqueous chlorine with this compound. Thus, it can be expected that the maximum reaction rate of chlorine with pentachlorophenol will occur at a pH somewhat less than 7, and that this reaction will be slower than the reaction of chlorine with less highly substituted phenols. Further, it is stated that in reacting with aqueous chlorine, phenol and the chlorophenols tend to undergo oxidative rupture of the benzene ring rather than substitution and that this tendency to rupture increases with more highly chlorinated phenolic reactants.

Figures 5, 6, and 7 show the reaction of aqueous chlorine with phenol and the chlorophenols with time. The initial chlorine dosage, using a stock chlorine solution prepared from gaseous chlorine, was 1.0 mg/l, the initial phenol concentration 50 mg/l, and the temperature 25° C. Figures 5, 6, and 7 represent the reactions at pH levels of 7, 8, and 9, respectively. A minimum reaction time of two hours was required before a significant decrease in total molar concentration of phenolic compounds occurred.

It should be remembered that these data represent the results of reactions in distilled water. The presence of ammonia, for instance, interferes significantly with the reaction of phenol with chlorine. Weil and Morris (28) indicate that for equal initial molar concentrations of ammonia and phenol at a pH of 8 and a temperature of 25° C, ammonia chlorinates to form NH_2CL about a thousand times faster than phenol chlorinates to form monochlorophenol. Therefore, the usefulness of the work of Lee is only qualitatively applicable to a discussion of chlorination of a heterogeneous wastewater.

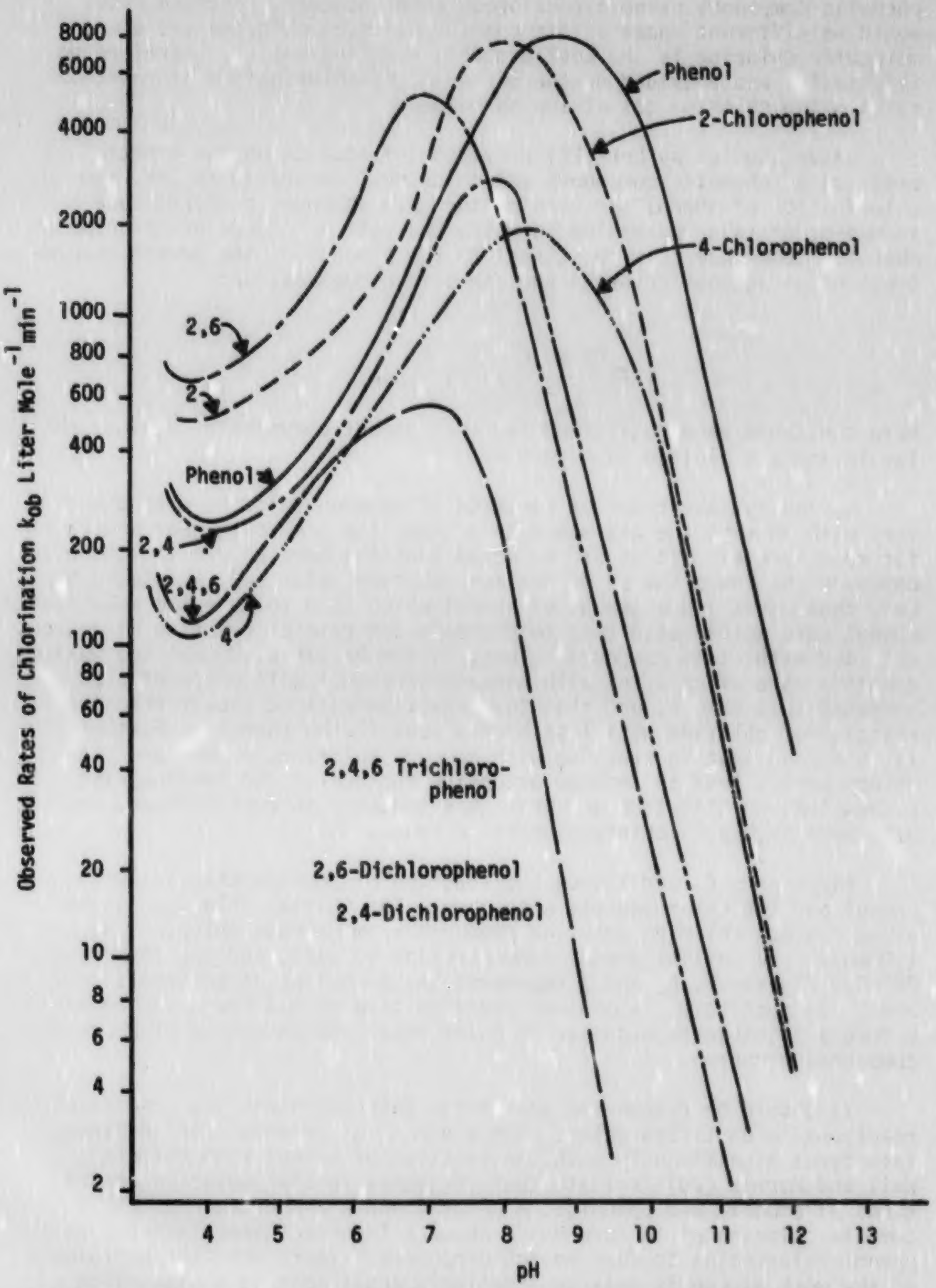

FIGURE 4. Observed Rates of Chlorination of Phenol and Chlorophenols

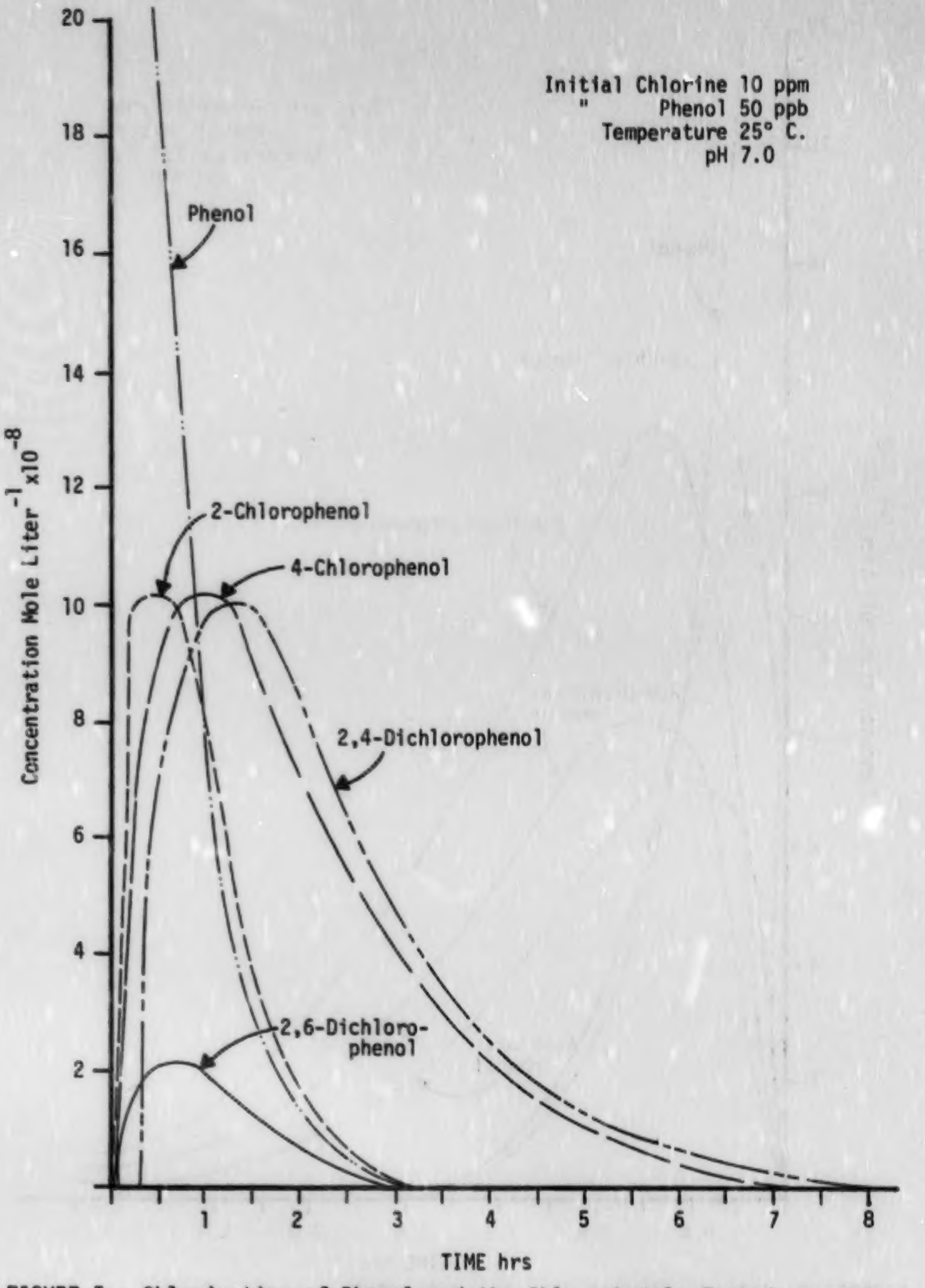

FIGURE 5. Chlorination of Phenol and the Chlorophenols Formed at pH 7.

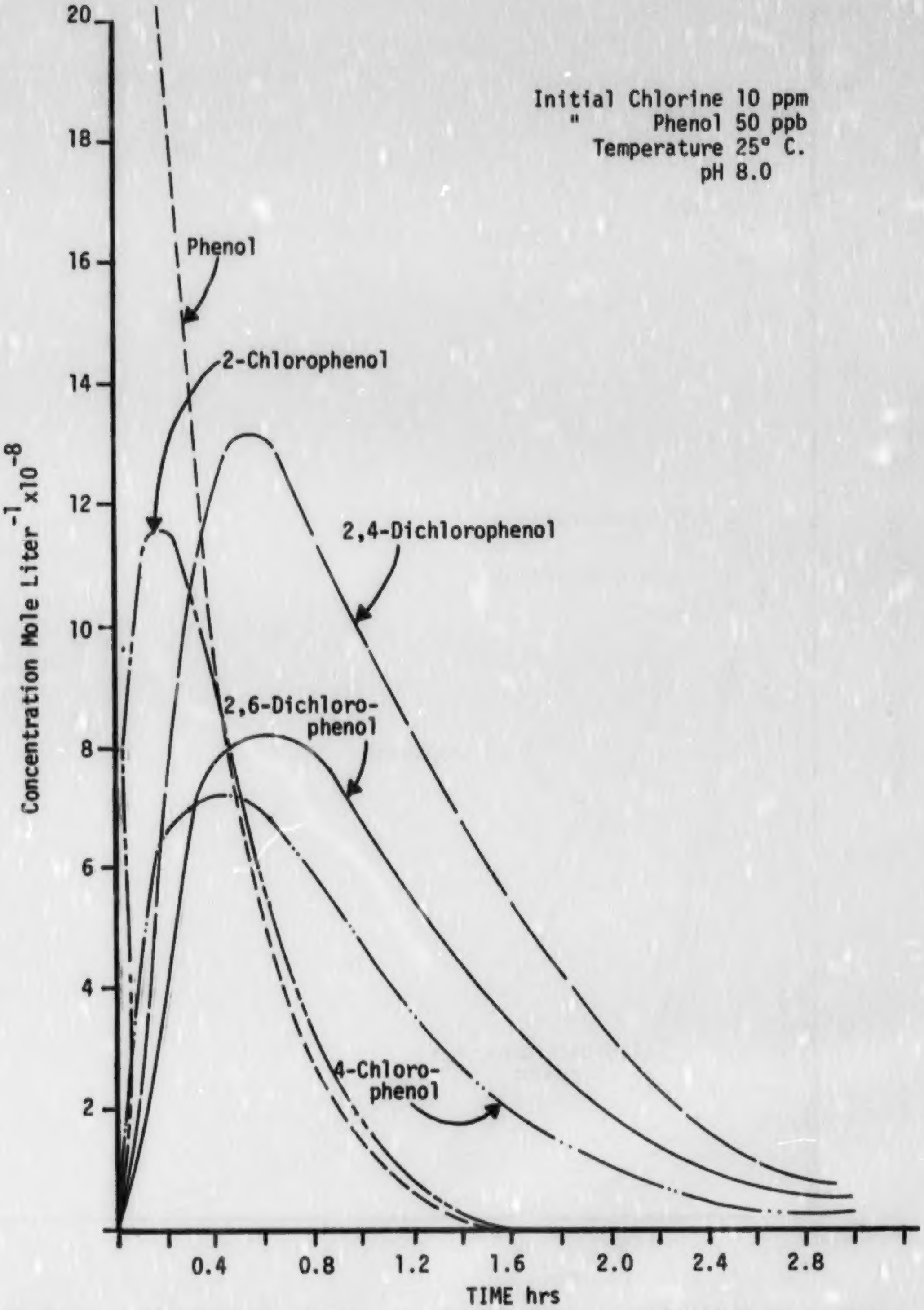

FIGURE 6. Chlorination of Phenol and the Chlorophenols formed at pH8.

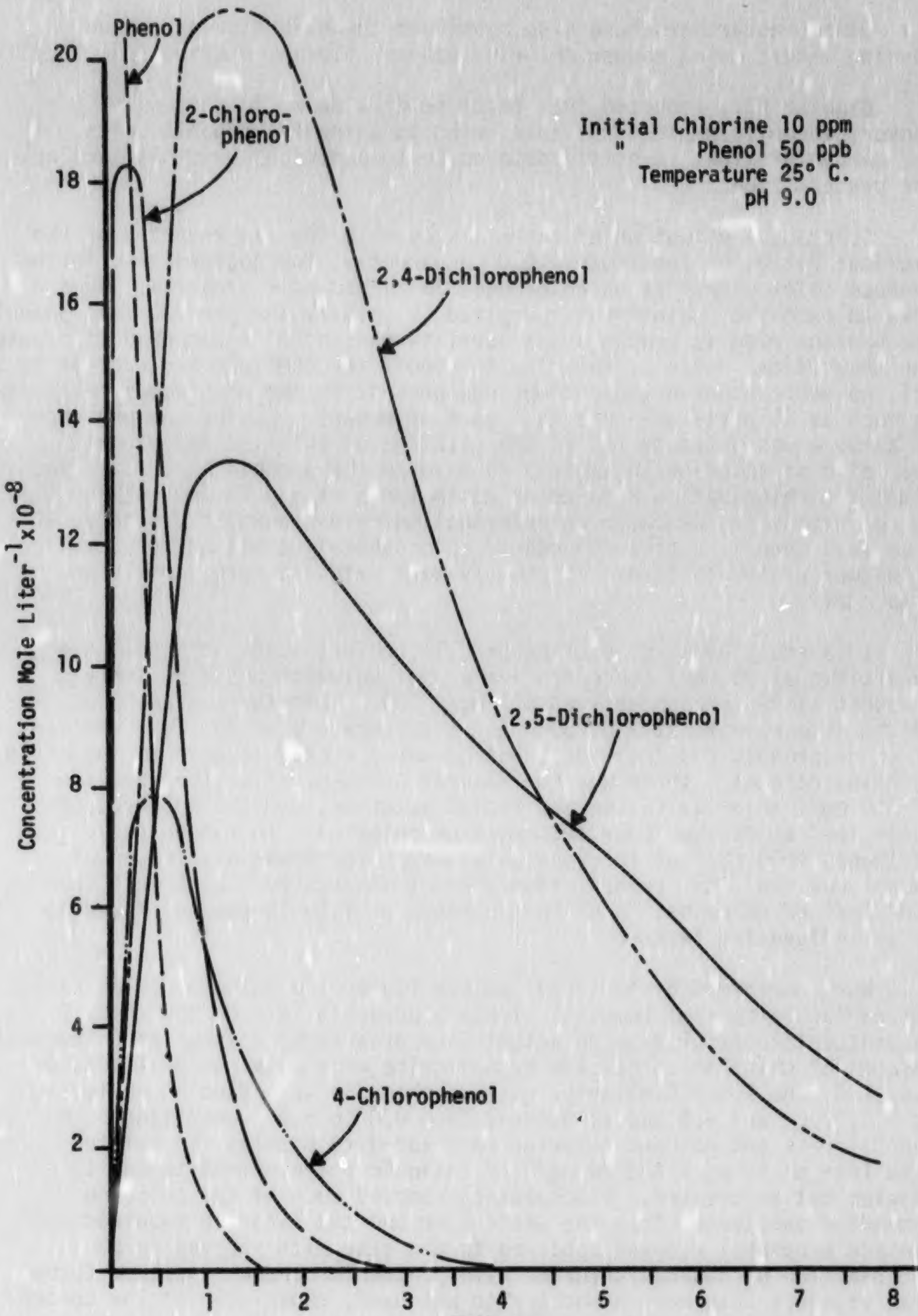

FIGURE 7. Chlorination of Phenol and the Chlorophenols Formed at pH 9.

Other researchers have also mentioned the oxidation of phenol bearing waters using either chlorine gas or chlorine dioxide (29, 30, 31).

Glabisz (31) reported that chlorine dioxide would successfully convert phenolic wastes from coke works to quinones, organic acids, and carbon dioxide. Specific data on test conditions were not available for presentation.

Successful oxidation of phenolics by chlorine was reported by the American Petroleum Institute (32). Apparently, low dosages of chlorine produce chlorophenolics which produce taste and odor problems. When a large excess of chlorine is supplied (5 grams/liter per 100 mg/l phenol), the benzene ring is broken and a harmless non-phenolic compound is created. The theoretical ratio of chlorine to phenol for complete destruction is 6:1; however, other organic compounds present in the wastewater necessitate as much as 50 parts chlorine to 1 part of phenol. Again, the presence of ammonia was noted to retard the reaction of chlorine and phenols. The ratio of chlorine to ammonia to oxidize the ammonia is 10:1. Reaction times for chlorination were reported in terms of one to several hours. In conformity to the observed chlorination rates shown in Figure 5, at a pH less than 7 a predominance of chlorophenolics was noticed, while at higher pH levels (above 7) phenols were oxidized more rapidly and completely.

In a study by H. R. Eisenhauer (22), chlorination was applied to an artificial 80 mg/l concentration phenol solution and a refinery effluent of 78 mg/l phenol and 627 mg/l COD. Chlorine was added as sodium hypochlorite at a pH of 4 and a temperature of 50° C. Creation of chlorophenols and their destruction was directly related to increasing chlorine dosages. There was no measurable phenol after the addition of 200 mg/l chlorine to the artificial solution, and the end products stabilized at dosages over 1000 mg/l of chlorine. In the refinery effluent, 1000 mg/l of chlorine were needed to remove all traces of phenol and the final chlorination product was achieved with less than 5000 mg/l of chlorine. A pH in the range of 4 to 10 was not found to be an influencing factor.

Work performed by Dust (33) substantiates the value of chlorination for pentachlorophenol removal. Table 5 presents data on the removal of pentachlorophenol from an actual wood preserving wastewater. Increasing dosages of chlorine as calcium hypochlorite were added at pH levels of 4.5, 7.0, and 9.5. Similarly, gaseous chlorine was added at pH levels of 4.5, 7.0, and 9.5 and at dosages from 0.0 to 5.0 grams/liter. The hypochlorite and gaseous chlorine were added to samples flocculated with lime at 18 mg/l and 20 mg/l of cationic polyelectrolyte and to samples not pretreated. Flocculation removed much of the chlorine demanding substances from the wastewater and the chlorine required for pentachlorophenol removed appeared to decrease with increasing pH. The reaction of gaseous chlorine with pentachlorophenol appeared to be less vigorous than when hypochlorite was used, especially at low concentrations (2.0 to 4.0 mg/l) of pentachlorophenol.

TABLE 5. EFFECT OF CHLORINATION OF PENTACHLOROPHENOL WASTE ON COD

Test Conditions	Available Chlorine (g/liter)	COD (mg/liter)
Calcium Hypochlorite pH = 4.5	0.0	24,200
	0.5	
	1.0	10,650
	1.5	
	2.0	10,600
	3.0	
	4.0	10,300
	5.0	
Calcium Hypochlorite pH = 7.0	0.0	23,800
	0.5	
	1.0	10,300
	1.5	
	2.0	10,200
	3.0	
	4.0	
	5.0	10,050
Chlorine Gas pH = 4.5	0.0	20,400
	0.5	
	1.0	
	1.5	
	2.0	10,250
	3.0	
	4.0	10,600
	5.0	
	10.0	10,200
Chlorine Gas pH = 7.0	0.0	23,600
	0.5	
	1.0	
	1.5	
	2.0	9,760
	3.0	
	4.0	10,700
	5.0	
	10.0	11,250

BIOLOGICAL TREATMENT

Activated Sludge

Cooke and Graham (34) performed laboratory scale studies on the biological degradation of phenolic wastes by the complete mixed activated sludge system. While many of the basic parameters needed for design such as MLSS were not presented, the final results were conclusive. The feed liquors contained phenols, thiocyanates, ammonia, and organic acids. Aeration varied from 8 to 50 hours. Influent concentration and percentage removal of phenol averaged 281 mg/l and 78 percent, respectively at a volumetric loading of 144 to 1600 kg/100 m^3 / day (9 to 100 lb/1000 ft^3 / day).

Badger and Jackman (35), studying bacteriological oxidation of phenols in aerated reaction vessels on a continuous flow basis, with a loading of approximately 1600 to 2400 kg/1000 m^3/day (100-150 lb phenol/1000 ft^3/day) and a MLSS of 2000 mg/l, found that with wastes containing up to 5000 mg/l phenol, a two day retention period could produce removal efficiencies in excess of 90 percent. Because the investigators were working with a coke gasification plant waste, the liquor contained thiocyanates. Higher oxidation efficiencies could be achieved with a reduction of the thiocyanate in the waste. Gas chromatography indicated no phenolic end products of degradation with original waste being a mixture of 36 percent monohydric and 64 percent polyhydric phenols.

Pruessner and Mancini (36) obtained a 99 percent oxidation efficiency for BOD in petrochemical wastes. Similarly, Coe (37) reported reductions of both BOD and phenols of 95 percent from petroleum wastes in bench-scale tests of the activated sludge process. Optimum BOD loads of 2247 kilograms/1000 m^3 per day (140 pounds/1000 ft^3 per day)were obtained. Coke plant effluents were successfully treated by Ludberg and Nicks (38), although some difficulty in start-up of the activated sludge system was experienced because of the high phenol content of the water.

The complete mixed, activated sludge process was employed to process a high-phenolic wastewater from a coal-tar distilling plant in Ontario (39). Initial phenol and COD concentrations of 500 and 6,000 mg/liter, respectively, were reduced in excess of 99 percent for phenols and 90 percent for COD.

Coal gas washing liquor was successfully treated by Nakashio (40) using activated sludge at a loading rate of 0.116 kg of phenol/kg MLSS/day. An influent phenol concentration of 1200 mg/l was reduced by more than 99 percent in this year-long study. Similar phenol removal rates were obtained by Reid and Janson (41), in treating wastewaters generated by the washing and decarbonization of aircraft engine parts. Other examples of biological treatment of phenolic wastes include work by Putilena (42), Meissner (43) and Shukov, et. al. (44).

Of particular interest is a specific test on the biological treatment of coke plant wastes containing phenols and various organics. In

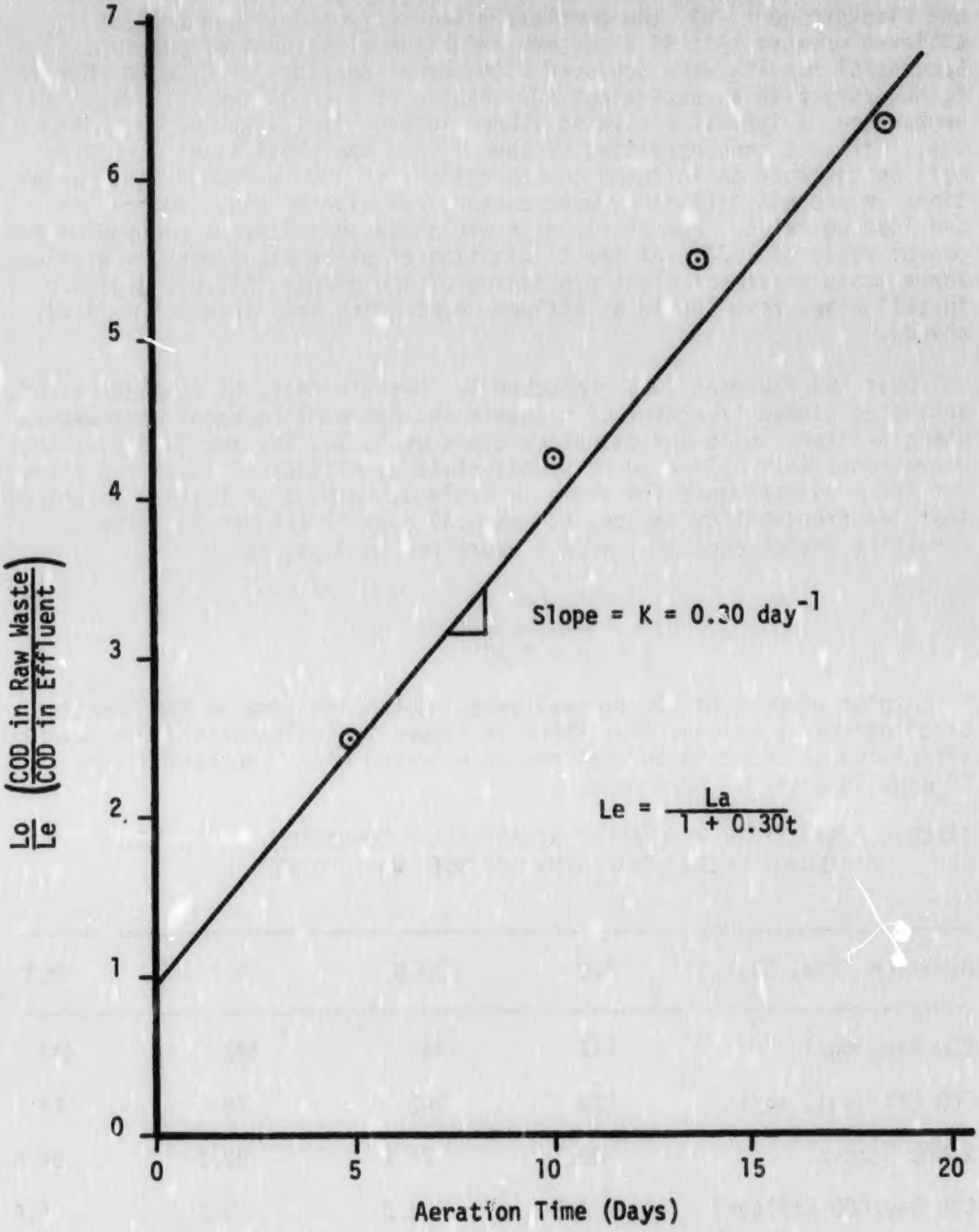

FIGURE 8. Determination of Reaction Rate Constant for a Creosote Wastewater

a report of pilot scale and full scale studies performed by Kostenbader and Flacksteiner (45), the complete mixed activated sludge process achieved greater than 99.8 percent oxidation efficiency of phenols. Successful results were achieved with phenol loadings of 0.86 kg phenol/kg MLSS/day with an equivalent BOD loading of 2 kg BOD/kg MLSS/day. In comparison, a typical activated sludge loading is 0.4 kg BOD/kg MLSS/day. Effluent concentrations of phenol from the pilot plant were 0.2 mg/l in contrast to influent concentrations of 3500 mg/l. Slight variations in process efficiency were encountered with varying temperatures and loading rates. Phosphoric acid was added to achieve a phosphorus-to-phenol ratio of 1:70. At the termination of pilot plant work, a similar large scale treatment plant processing of 424 m^3/day (112,000 gpd) was installed and resulted in an effluent containing less than 0.1 mg/l of phenol.

Dust and Thompson (46) conducted bench-scale tests of complete-mixed, activated sludge treatment of creosote and pentachlorophenol wastewaters using 5-liter units and detention times of 5, 10, 15, and 20 days. The operational data collected at steady-state conditions of substrate removal for the creosote waste are shown in Table 6. A plot of these data showed that the treatability factor, K, was 0.30 days $^{-1}$ (Figure 8). The resulting design equation, with t expressed in days, is:

$$Le = \frac{Lo}{1 + 0.30^{t}}$$

A plot of percent COD removal versus detention time in the aerator based on the above equation, shown in Figure 9, indicates that an oxidation efficiency of about 90 percent can be expected with a detention time of 20 days in units of this type.

TABLE 6. SUBSTRATE REMOVAL AT STEADY-STATE CONDITIONS IN ACTIVATED SLUDGE UNITS CONTAINING CREOSOTE WASTEWATER

Aeration Time, Days	5.0	10.0	14.7	20.1
COD Raw, mg/l	447	447	442	444
COD Effluent, mg/l	178	103	79	67
% COD Removal	60.1	76.9	82.2	84.8
COD Raw/COD Effluent	2.5	4.3	5.6	6.6

Work was conducted to determine the degree of biodegradability of pentachlorophenol waste. Cultures of bacteria prepared from soil removed from a drainage ditch containing pentachlorophenol waste were used to inoculate the treatment units. Feed to the units contained 10 mg/liter

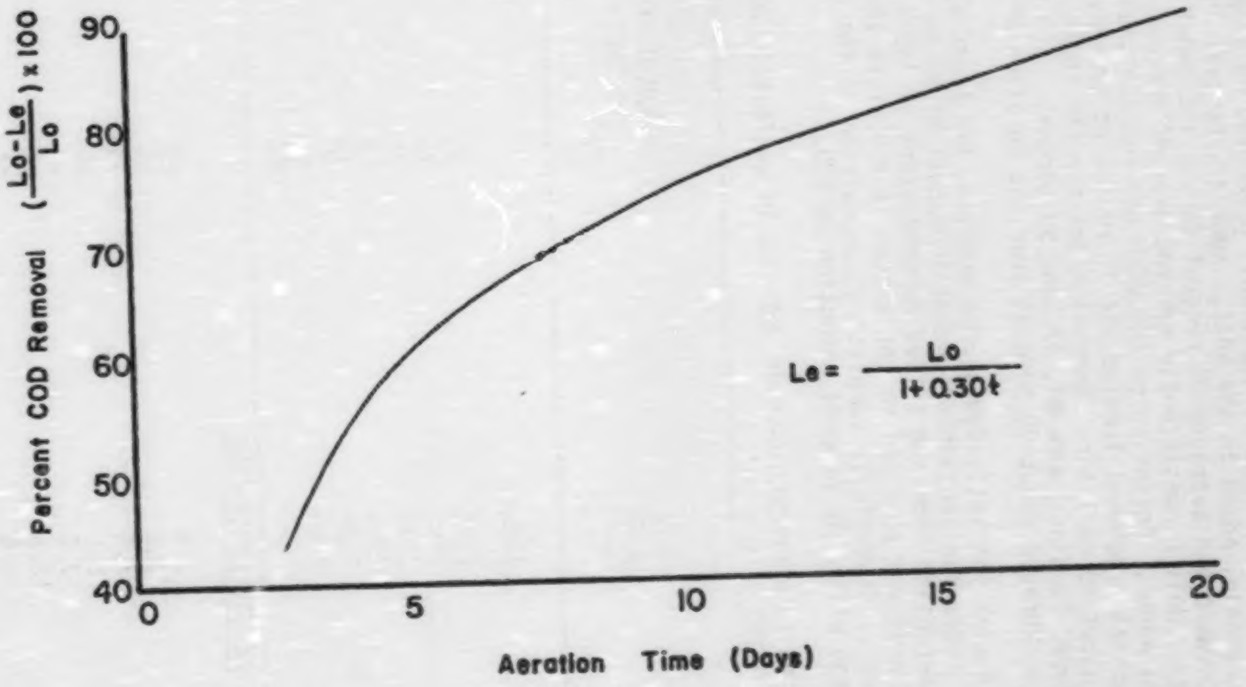

FIGURE 9.
COD Removal from a Creosote Wastewater by Aerated Lagoon without Sludge Return

of pentachlorophenol and 2,400 mg/liter COD. For the two 5-liter units (A and B) the feed was 500 and 1000 ml/day and detention times were, in order, 10 and 5 days. Removal rates for pentachlorophenol and COD are given in Table 7. For the first 20 days, Unit A removed only 35 percent of the pentachlorophenol added to the unit. However, removal increased dramatically afterward and averaged 94 percent during the remaining 10 days of the study. Unit B consistently removed over 90 percent of the pentachlorophenol added. Beginning on the 46th day and continuing through the 51st day, pentachlorophenol loading was increased at two-day intervals to a maximum of about 59 mg/liter. Removal rates for the three two-day periods of increased loadings were 94, 97, and 99 percent. COD removal for the two units averaged about 90 percent over the duration of the study.

Also working with the activated sludge process, Kirsh and Etzel (47) obtained removal rates for pentachlorophenol in excess of 97 percent using an 8-hour detention time and a feed concentration of 150 mg/liter. The pentachlorophenol was supplied to the system in a mixture that included 100 mg/liter phenol. Essentially complete decomposition of the phenol was obtained, along with a 92 percent reduction in COD.

TABLE 7. REDUCTION IN PENTACHLOROPHENOL AND COD IN WASTEWATER TREATED IN ACTIVATED SLUDGE UNITS

DAYS	RAW WASTE (mg/l)	EFFLUENT FROM UNIT (% Removal) "A"	"B"
	COD		
1-5	2350	78	78
6-10	2181	79	79
11-15	2735	76	75
16-20	2361	82	68
21-25	2288	90	86
26-30	2490	--	84
31-35	2407	83	80
	PENTACHLOROPHENOL		
1-5	7.9	20	77
6-10	10.2	55	95
11-15	7.4	33	94
16-20	6.6	30	79
21-25	7.0	--	87
26-30	12.5	94	94
31-35	5.8	94	91
36-40	10.3	--	91
41-45	10.0	--	96
46-47	20.0	--	95
48-49	30.0	--	97
50-51	40.0	--	99

Cooper and Catchpole (48) reported greater than 95 percent oxidation of phenols using activated sludge units treating coke plant effluents containing phenols, thiocyanates, and sulfides. Adequate data were not available on the detailed operating parameters of the activated sludge plant.

Trickling Filters

Hsu, Yany, and Weng (49) reported successful treatment of coke plant phenolic wastes with a trickling filter, removing over 80 percent of the phenols. It was stated that influent phenol concentrations should not exceed 100 mg/l.

Using a Surfpac trickling filter, Francingues (50) was able to remove 80 to 90 percent of the influent phenol from a wood preserving creosote wastewater at a loading rate of about 16 kg/1000 m^3/day (1 lb phenol/1000 ft^3/day).

Sweets, Hamdy, and Weiser (51) studied the bacteria responsible for phenol reductions in industrial waste and reported good phenol removal from synthesized waste containing concentrations of 400 mg/l. Reductions of 23 to 28 percent were achieved in a single pass of the wastewater through a pilot trickling filter having a filter bed only 30 centimeters (12 inches) deep.

Waters containing phenol concentrations of up to 7500 mg/l were successfully treated in laboratory tests conducted by Reid and Libby (52). Phenol removals of 80 to 90 percent were obtained for concentrations on the order of 400 mg/l. Their work confirmed that of Ross and Shepard (53), who found that strains of bacteria isolated from a trickling filter could survive phenol concentrations of 1600 mg/liter and were able to oxidize phenols in concentrations of 450 mg/liter at better than 99 percent efficiency. Reid, Wortman, and Walker (54) found that many pure cultures of bacteria were able to live in phenol concentrations of up to 200 mg/l, but few survived concentrations above 900 mg/l, although some were grown in concentrations as high as 3700 mg/l.

Harlow, Shannon, and Sercu (55) described the operation of a commercial-size trickling filter containing "Dowpac" filter medium that was used to process wastewater containing 25 mg/l phenol and 450 to 1900 mg/l BOD. Reductions of 96 percent for phenols and 97 percent for BOD were obtained in this unit. Their results compare favorably with those reported by Montes, Allen, and Schowell (56) who obtained BOD reductions of 90 percent in a trickling filter using a 1:2 recycle ratio, and Dickerson and Laffey (57), who obtained phenol and BOD reductions of 99.9 and 96.5 percent, respectively, in a trickling filter used to process refinery wastewater.

A combination biological waste-treatment system employing a trickling filter and an oxidation pond was reported on by Davies, Biehl, and Smith (58). The filter, which was packed with a plastic medium, was used for a roughing treatment of 10.6 million liters (2.8 million gallons) of wastewater per day, with final treatment occurring in the oxidation pond. Removal rates of 95 percent for phenols and 60 percent for BOD were obtained in the filter, notwithstanding the fact that the pH of the influent averaged 9.5.

A study of biological treatment of refinery wastewaters by Austin, Meehan, and Stockham (59) employed a series of four trickling filters with each filter operating at a different recycle ratio. The waste contained 22 to 125 mg/liter of oil and this adversely affected BOD removal. However, phenol removal was unaffected by oil concentrations within the range studies.

Prather and Gaudy (60) found that significant reductions of COD, BOD, and phenol concentrations in refinery wastewater were achieved by simple aeration treatments. They concluded that this phenomenon accounted for the high allowable loading rates for biological treatments such as trickling filtration.

The practicality of using trickling filters for secondary treatment of wastewaters from the wood preserving industry was explored by Dust and Thompson (46). Creosote wastewater was applied at BOD loading rates of from 400 to 3050 kilograms/1000 m^3 per day (25 to 190 pounds/1000 ft^3 per day) to a pilot unit containing a 6.4 meter (21 feet) filter bed of plastic media. The corresponding phenol loadings were 1.6 to 54.6 kilograms/1000 m^3 per day (0.1 to 3.4 pounds/1000 ft^3 per day). Raw feed-to-recycle ratios varied from 1:7 to 1:28. Daily samples were analyzed over a period of seven months that included both winter and summer operating conditions. Because of wastewater characteristics at the particular plant cooperating in the study, the following pretreatment steps were necessary: (a) equalization of wastes; (b) primary treatment by coagulation for partial solids removal; (c) dilution of the wastewater to obtain BOD loading rates commensurate with the range of raw flow levels provided by the equipment; and (d) addition to the raw feed of supplementary nitrogen and phosphorus. Dilution ratios of 0 to 14 were used.

The efficiency of the system was essentially stable for BOD loadings of less than 1200 kilograms/1000 m^3 per day (75 lbs/1000 ft^3 per day). The best removal rate was achieved when the hydraulic application rate was 2.85 lpm/m^2 (0.07 gpm/ft^2) of raw waste and 40.7 lpm/m^2 (1.0 gpm/ft^2) of recycled waste. The COD, BOD, and phenol removals obtained under these conditions are given in Table 8. Table 9 shows the relationship between BOD loading rate and removal efficiency. BOD removal efficiency at loading rates of 1060 kilograms/1000 m^3 per day (66 pounds/1000 ft^3 per day) was on the order of 92 percent, and was not improved at reduced loadings. Comparable values for phenols at loading rates of 19.3 kilograms/1000 m^3 per day (1.2 pounds/1000 ft^3 per day) were about 97 percent.

Since phenol concentrations were more readily reduced to levels compatible with existing standards than were BOD concentrations, the sizing of commercial units was based on BOD removal rates. Various combinations of filter-bed depths, tower diameters, and volumes of filter media that were calculated to provide a BOD removal rate of 90 percent for an influent having a BOD of 1500 mg/liter are shown in Table 10 for a plant with a flow rate of 75,700 lpd (20,000 gpd).

TABLE 8. BOD, COD, AND PHENOL LOADING AND REMOVAL RATES FOR PILOT TRICKLING FILTER PROCESSING A CREOSOTE WASTEWATER

Measurement	Characteristics		
	BOD	COD	Phenol
Raw Flow Rate lpm/m^2 (gpm/ft^2)	2.85 (0.07)	2.85 (0.07)	2.85 (0.07)
Recycle Flow Rate lpm/m^2 (gpm/ft^2)	40.7 (1.0)	40.7 (1.0)	40.7 (1.0)
Influent Concentration (mg/l)	1698	3105	31
Loading Rate gm/m^3/day	1075 (66.3)	1967 (121.3)	19.5 (1.2)
Effluent Concentration (mg/l)	137	709	<1.0
Removal (%)	91.9	77.0	99+

TABLE 9. RELATIONSHIP BETWEEN BOD LOADING AND TREATABILITY FOR PILOT TRICKLING FILTER PROCESSING A CREOSOTE WASTEWATER

BOD Loading kg/cu m	BOD Loading (lb/cu ft./day)	Removal (%)	Treatability Factor[a]
373	(23)	91	0.0301
421	(26)	95	0.0383
599	(37)	92	0.0458
859	(53)	93	0.0347
1069	(66)	92	0.0312
1231	(76)	82	0.0339
1377	(85)	80	0.0286
1863	(115)	75	0.0182
2527	(156)	62	0.0130

[a] Based on the equation:

$$\frac{Le}{Lo} = e^{KD/Q^{0.5}} \quad \text{(Germain, 1966)}$$

in which Le = BOD concentration of settled effluent, Lp = BOD of feed, Q = hydraulic application rate of raw waste in gpm/ft^2, D = depth of media in feet, and K = treatability factor (rate coefficient).

TABLE 10. SIZING OF TRICKLING FILTER FOR A WOOD PRESERVING PLANT

(NOTE: Data are based on a flow rate of 75,700 liters per day (20,000 gallons per day), with filter influent BOD of 1500 and effluent BOD of 150 mg/l).

Depth of filter bed m (ft)	Raw Flow lpm/m^2 (gpm/ft^2) filter surface)	Recycle flow lpm/m^2 (gpm/ft^2) filter surface)	Filter Surface area m^2 (ft^2)	Tower dia m (ft)	Volume of media m^3 (ft^3)
3.26 (10.7)	0.774 (0.019)	29.7 (0.73)	65.8 (708)	9.14 (30.0)	213 (7617)
3.81 (12.5)	1.059 (0.206)	29.3 (0.72)	48.3 (520)	7.83 (25.7)	183 (6529)
4.36 (14.3)	1.385 (0.034)	28.9 (0.71)	37.0 (398)	6.86 (22.5)	160 (5724)
4.91 (16.1)	1.793 (0.044)	28.5 (0.70)	29.3 (315)	6.10 (20.0)	142 (5079)
5.46 (17.9)	2.200 (0.054)	28.1 (0.69)	23.7 (255)	5.49 (18.0)	128 (4572)
5.97 (19.6)	2.648 (0.065)	27.7 (0.68)	19.5 (210)	4.97 (16.3)	116 (4156)
6.52 (21.4)	3.178 (0.078)	27.3 (0.67)	16.4 (177)	4.57 (15.0)	107 (3810)

Oxidation Ponds

The American Petroleum Institute's "Manual on Disposal of Refinery Wastes" (61) refers to several industries that have successfully used oxidation ponds to treat phenolic wastes. Montes (62) reported on results of field studies involving the treatment of petrochemical wastes using oxidation ponds. He obtained BOD reductions of 90 to 95 percent in ponds loaded at the rate of 84 kilograms of BOD per hectare per day (75 pounds/acre/day).

Phenol concentrations of 990 mg/liter in coke oven effluents were reduced to about 7 mg/liter in field studies of oxidation ponds conducted by Biczyski and Suschka (63). Similar results have been reported by Skogen (64) for a refinery waste.

The literature contains operating data on only one pond used for treating wastewater from wood preserving operations (65, 66, 67). This is the oxidation pond used as part of a waste treatment system by Weyerhaeuser Company at its DeQueen, Arkansas, wood preserving plant. As originally designed and operated in the early 1960's, the DeQueen waste treatment system consisted of holding tanks into which water from the oil-recovery system flowed. From the holding tanks the water was sprayed into a terraced hillside from which it flowed into a mixing chamber adjacent to the pond. Here it was diluted 1:1 with creek water, fortified with ammonia and phosphates, and discharged into the pond proper. Retention time in the pond was 45 days. The quality of the effluent was quite variable, with phenol content ranging up to 40 mg/liter. In 1966, the system was modified by installing a raceway containing a surface aerator and a settling basin in a portion of the pond. The discharge from the mixing chamber now enters a raceway where it is treated with a flocculating agent. The floc formed collects in the settling basin. Detention time is 48 hours in the raceway and 18 hours in the settling basin from which the wastewater enters the pond proper.

These modifications in effect changed the treating system from an oxidation pond to a combination aerated lagoon and polishing pond. The effect on the quality of the effluent was dramatic. Figure 10 shows the phenol content at the outfall of the pond before and after installation of the aerator. As shown by these data, phenol content decreased abruptly from an average of about 40 mg/liter to 5 mg/liter.

Even with the modifications described, the efficiency of the system remains seasonally dependent. Table 11 give phenol and BOD values for the pond effluent by month for 1968 and 1970. The smaller fluctuations in these parameters in 1970 as compared with 1968 indicate a gradual improvement in the system.

Soil Irrigation

The principal feature of the soil irrigation method of wastewater treatment is its simplicity. Water that has been freed of surface oils and, depending upon the presence of emulsified oils, treated with flocculated chemicals and filtered through a sand bed is simply sprayed onto a prepared field. Soil microorganisms decompose the organic matter in the water in much the same fashion as occurs in more conventional waste treatment systems.

In addition to its simplicity, soil irrigation has the advantage of low capital investment (exclusive of land costs), low operating and maintenance costs, requires a minimum of mechanical equipment,

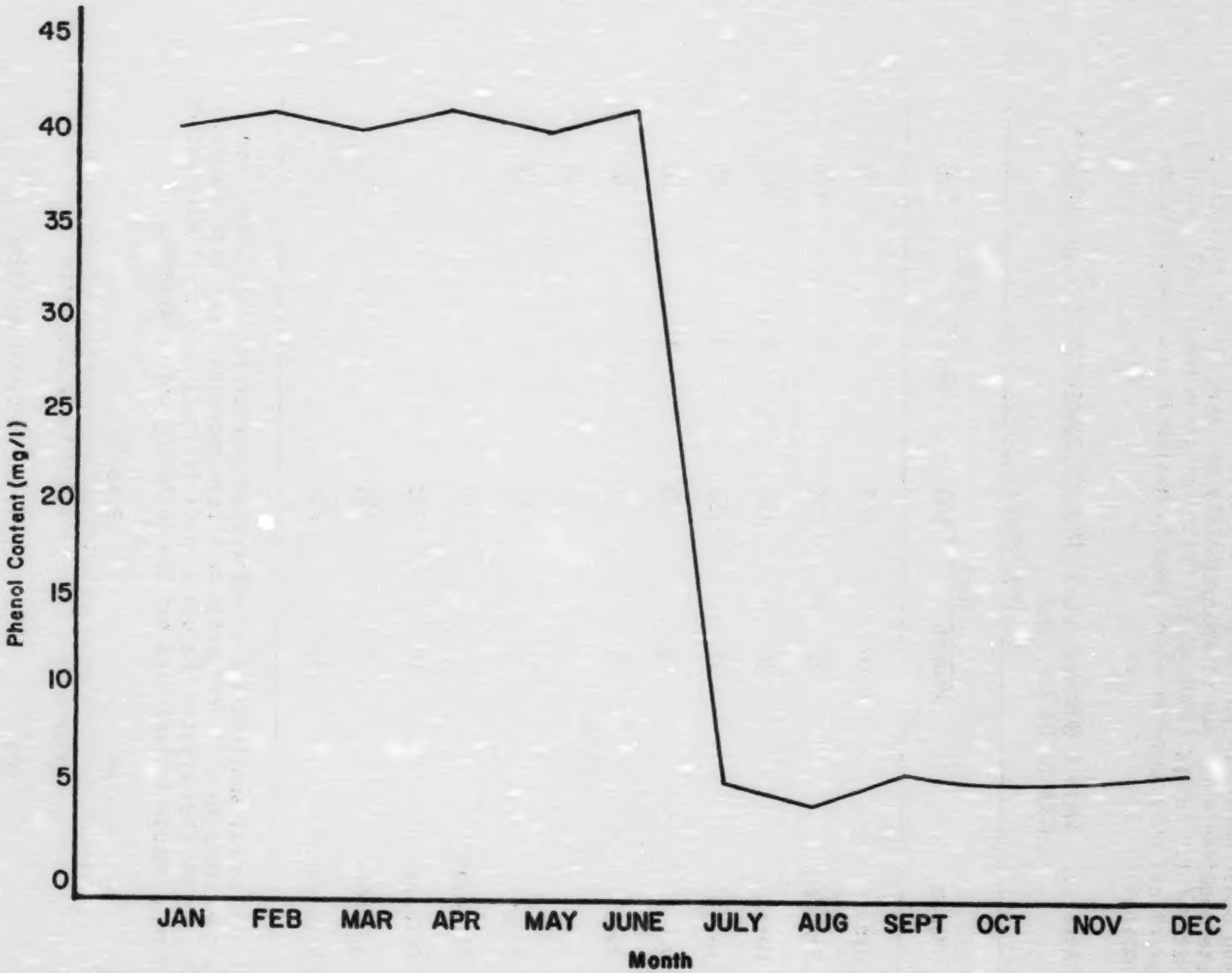

Figure 10. Phenol Content in Oxidation Pond Effluent Before and After Installation in June 1966 of Aerator

and produces a high-quality effluent in terms of color, oxygen demand, and other pertinent parameters. Its chief disadvantage is that its use requires a minimum of approximately one acre for an application rate of 13,250 lpd (3500 gpd). This limitation makes soil irrigation practical only in areas where land is available and relatively inexpensive.

TABLE 11. AVERAGE MONTHLY PHENOL AND BOD CONCENTRATIONS IN EFFLUENT FROM OXIDATION POND
(mg/liter)

Month	1968 Phenol	1968 BOD	1970 Phenol	1970 BOD
January	26	290	7	95
February	27	235	9	140
March	25	190	6	155
April	11	150	3	95
May	6	100	1	80
June	5	70	1	60
July	7	90	1	35
August	7	70	1	45
September	7	110	1	25
October	16	150	-	-
November	7	155	-	-
December	11	205	-	-

Several applications of wastewaters containing high phenol concentrations to soil irrigation have been reported. One such report, by Fisher (68) related the use of soil irrigation to treat wastewaters from a chemical plant that had the following characteristics:

pH	9 to 10
Color	5,000 to 42,000 units
COD	1,600 to 5,000 mg/liter
BOD	800 to 2,000 mg/liter

Operating data from a 0.81 hectare (2 acre) field, when irrigated at a rate of 7570 liters (2,000 gal) per acre/day for a year, showed color removal of 88 to 99 percent and COD removal of 85 to 99 percent.

The same author reported on the use of this method to treat effluent from two tar plants that contained 7,000 to 15,000 mg/liter phenol and 20,000 to 54,000 mg/liter COD. The waste was applied to the field at a rate of about 9460 liters (2500 gal) per acre/day. Water leaving the area had COD and phenol concentrations of 60 and 1 mg/liter, respectively. Based on the lower influent concentration for each parameter, these values represent oxidation efficiencies of well over 99 percent for both phenol and COD.

Bench-scale treatment of coke plant effluent by soil irrigation was also studied by Fisher. Wastes containing BOD and phenol concentrations of 5,000 and 1,550 mg/liter, respectively, were reduced by 95+ and 99+ percent when percolated through 0.9 meters (36 inches) of soil. Fisher pointed out that less efficient removal was achieved with coke-plant effluents using the activated sludge process, even when the waste was diluted with high-quality water prior to treatment. The effluent from the units had a color rating of 1,000 to 3,000 units, compared to 150 units for water that had been treated by soil irrigation.

Both laboratory and pilot scale field tests of soil-irrigation treatments of wood preserving wastewater were conducted by Dust and Thompson (46). In the laboratory tests, 210-liter (55 gallon) drums containing a heavy clay soil 60-centimeters (24 inches) deep were loaded at rates of 32,8000, 49,260, and 82,000 liters/hectare/day (3,500, 5,250, and 8,750 gallons/acre/day). Influent COD and phenol concentrations were 11,500 and 150 mg/liter, respectively. Sufficient nitrogen and phosphorus were added to the waste to provide a COD:N:P ratio of 100:5:1. Weekly effluent samples collected at the bottom of the drums were analyzed for COD and phenol.

Reductions of more than 99 percent in COD content of the wastewater were attained from the first week in the case of the two highest loadings and from the fourth week for the lowest loading. A breakthrough occurred during the 22nd week for the lowest loading rate and during the fourth week for the highest loading rate. The COD removal steadily decreased thereafter for the duration of the test. Phenol removal showed no such reduction, but instead remained high throughout the test. The average test results for the three loading rates are given in Table 12. Average phenol removal was 99+ percent. Removal of COD exceeded 99 percent prior to breakthrough and averaged over 85 percent during the last week of the test.

The field portion of Dust and Thompson's (46) study was carried out on an 0.28-hectare (0.8 acre) plot prepared by grading to an approximately uniform slope and seeded to native grasses. Wood preserving wastewater from an equalization pond was applied to the field at the rate of 32,800 liters/hectare/day (3,500 gallons/acre/day) for a period of nine months. Average monthly influent COD and phenol concentrations ranged from 2,000 to 3,800 mg/liter and 235 to 900 mg/liter, respectively. Supplementary nitrogen and phosphorus were not added. Samples for analyses were collected weekly at soil depths of 0 (surface), 30, 60, and 120 centimeters (1, 2, and 4 feet).

The major biological reduction in COD and phenol content occurred at the surface and in the upper 30 centimeters (1 foot) of soil. A COD reduction of 55.0 percent was attributed to overland flow. The comparable reduction for phenol content was 55.4 percent (Table 13). COD reductions at the three soil depths, based on raw waste to the field, were 94.9, 95.3, and 97.4 percent, respectively, for the 30-, 60-, and 120 centimeter (1-, 2-, and 4-foot) depths. For phenols, the reductions were, in order, 98.9, 99.2, and 99.6 percent.

TABLE 12. RESULTS OF LABORATORY TESTS OF SOIL IRRIGATION METHOD OF WASTEWATER TREATMENT[a]

Loading Rate (Liter/ha/day)	Length of Test (Week)	Avg. & COD Removal to Breakthrough	COD REMOVAL Last Week of Test %	Phenol Avg. % Removal (All Weeks)
32,800 (3,500)	31	99.1 (22 wks)	85.8	98.5
49,260 (5,250)	13	99.6	99.2	99.7
82,000 (8,750)	14	99.0 (4 wks)	84.3	99.7

Loading rates in parentheses in gallons/acre/day

[a] Creosote wastewater containing 11,500 mg/liter of COD and 150 mg/liter of phenol was used.

Activated Carbon Filtration

Activated carbon is used commercially to treat petroleum (69) and other types (70) of industrial wastewaters. It can also be used effectively to remove phenolic compounds from wood preserving waste streams. Although carbon has a strong affinity for nonpolar compounds such as phenols, adsorption is not limited to these materials. Other organic materials in wastewater are also adsorbed, resulting in a decrease in the total oxygen demand of the waste. Because the concentration of the latter substances exceeds that of phenols in effluents from wood preserving plants, the useful life of activated carbon is determined by the concentration of these materials and the rate at which they are adsorbed.

TABLE 13. REDUCTION OF COD AND PHENOL CONTENT IN WASTEWATER TREATED BY SOIL IRRIGATION

Month	Raw Waste	Soil Depth (centimeters)			
		0	30	60	120
		COD (mg/l)			
July	2235	1400	--	--	66
August	2030	1150	--	--	64
September	2355	1410	--	--	90
October	1780	960	150	--	61
November	2060	1150	170	170	46
December	3810	670	72	91	58
January	2230	940	121	127	64
February	2420	580	144	92	64
March	2460	810	101	102	68
April	2980	2410	126	--	76
Average % Removal (weighted)		55.0	94.9	95.3	97.4
		Phenol (mg/l)			
July	235	186	--	--	1.8
August	512	268	--	--	0.0
September	923	433	--	--	0.0
October	310	150	4.6	--	2.8
November	234	86	7.7	3.8	0.0
December	327	6	1.8	9.0	3.8
January	236	70	1.9	3.8	0.0
February	246	111	4.9	2.3	1.8
March	277	77	2.3	1.9	1.3
April	236	172	1.9	0.0	0.8
Average % Removal (weighted)		55.4	98.9	99.2	99.6

Results of carbon-adsorption studies conducted by Dust and Thompson (46) on a creosote wastewater are shown in Figure 11. Granular carbon was used and the contact time was 24 hours. The wastewater was flocculated with ferric chloride and its pH adjusted to 4.0 prior to exposure to the carbon. As shown in the figure, 96 percent of the phenols and 80 percent of the COD were removed from the wastewater at a carbon dosage of 8 g/liter. The loading rate dropped off sharply at that point, and no further increases in phenol removal and only small increases in COD removal occurred by increasing carbon dosage to 50 gm/liter. Similar results were obtained in tests using pentachlorophenol wastewater.

Results of adsorption isotherms that were run on pentachlorophenol wastewater, and other samples of creosote wastewater followed a pattern similar to that shown in Figure 11. In some instances a residual content of phenolic compounds remained in wastewater after a contact period of 24 hours with the highest dosage of activated carbon employed, while in other instances all of the phenols were removed. Loading rates of 0.16 kilograms of phenol and 1.2 kilograms of COD per kilogram of carbon were typical, but much lower rates were obtained with some wastewaters.

Miscellaneous Treatment and Handling Methods

Wastes from wood preserving plants may also be handled by containment, if adequate land is available, by spray evaporation, if a relatively high operating cost can be tolerated, or by heat evaporation or incineration if the waste stream is small.

SUMMARY

It was concluded that previous laboratory and pilot work demonstrated that chemical or biological action could be used to reduce wastewater pentachlorophenol concentration. Pentachlorophenol is more toxic than simple creosote but less soluble in water. High concentrations of pentachlorophenol can be oxidized to harmless, biodegradable chloranyls. Low concentration of pentachlorophenol, on the order of 10 to 30 mg/l, can be degraded biologically in the presence of relatively numerous nutrients. Some portion of the Carbondale plant's wastewater could, therefore, be degraded in an activated sludge system, probably including the pnetachlorophenol and creosote fractions.

Ample evidence was found in the literature to substantiate destructive chlorination and biological oxidation of phenolic compounds. Thus, while there remained some ambiguity concerning the detailed operating parameters for a treatment plant for these wastes, the basic processes were sound. It was felt that early ambiguities arose from non-parametric studies with varying feed waters, few of which were specifically wood preserving wastewaters. It was the intent of the Carbondale study to clarify the various operating parameters and provide a sound basis for future design work.

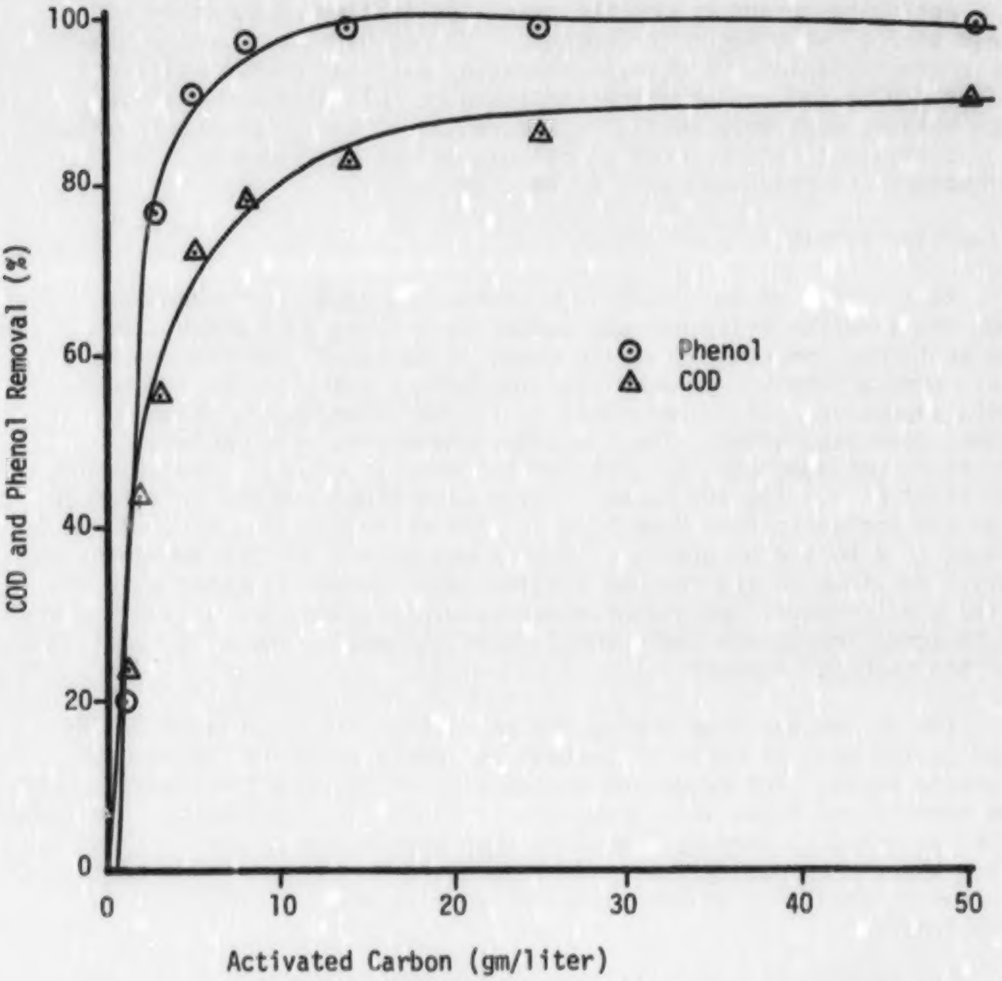

FIGURE 11
Relationship Between Weight of Activated Carbon
Added and Removal of COD and Phenols from a Creosote Wastewater

SECTION V

MATERIALS AND METHODS

Following acceptance of the grant application, laboratory and field studies were begun in Carbondale to establish wastewater flow and characteristics. A mobile laboratory was stationed on-site for a five day period during which samples were collected and analyzed. Flow measurements were initiated and continued for a two month period. A discussion of data collection methods and of development of design parameters are presented in this section.

PRE-DESIGN STUDIES

At the time of the pre-design wastewater studies, condensate from the treating cylinders was pumped to primary separation tanks. The pentachlorophenol condensate which is isolated from the creosote waste stream receives polymer addition before going to the secondary penta separator. Since penta-oil is lighter than water, skimming allows good separation. The creosote condensate, after polymer addition, was separated by settling the heavier creosote and skimming the light oils. The two waste streams were then combined in a common sump and pumped to Pond 2 or Pond 3. The effluents from Ponds 2 and 3 flowed to a Pond 4 by gravity. Pond 1 was maintained for emergency use only. Previous to the present design, these ponds, together with the primary oil removal and preservation recovery system and a 1.05 hectare (2.58 acre) irrigation field constituted the waste treatment facilities for the Carbondale plant.

The wastewater flow during the pre-design study averaged 27,055 l pd (7,148 gpd) of which 36 percent was penta waste and 64 percent creosote waste. The range and variability of the total wastestream and the constituent flows is illustrated in Figure 12. Obviously, the flowrate was erratic, varying from less than one-fourth to nearly three times the average daily flow. Of importance is the fact that penta flow was non-existent for several consecutive days and then occurred in slug flows.

The analytical data collected during the five day sampling period is presented in Table 14. Each pond was sampled during this period; however, due to inplant modifications, it was decided that the pond data was of little value for design. The samples considered to be of value were those from the creosote decantor effluent and the common sump. During the period of sampling, there was no flow for at least two days from the penta separator and, therefore, the concentrations determined in the commom sump are not necessarily average concentrations. A better estimate of average conditions is obtained by calculating concentrations based on the preparation of average flow from each waste source. This calculated average is also shown in Table 14.

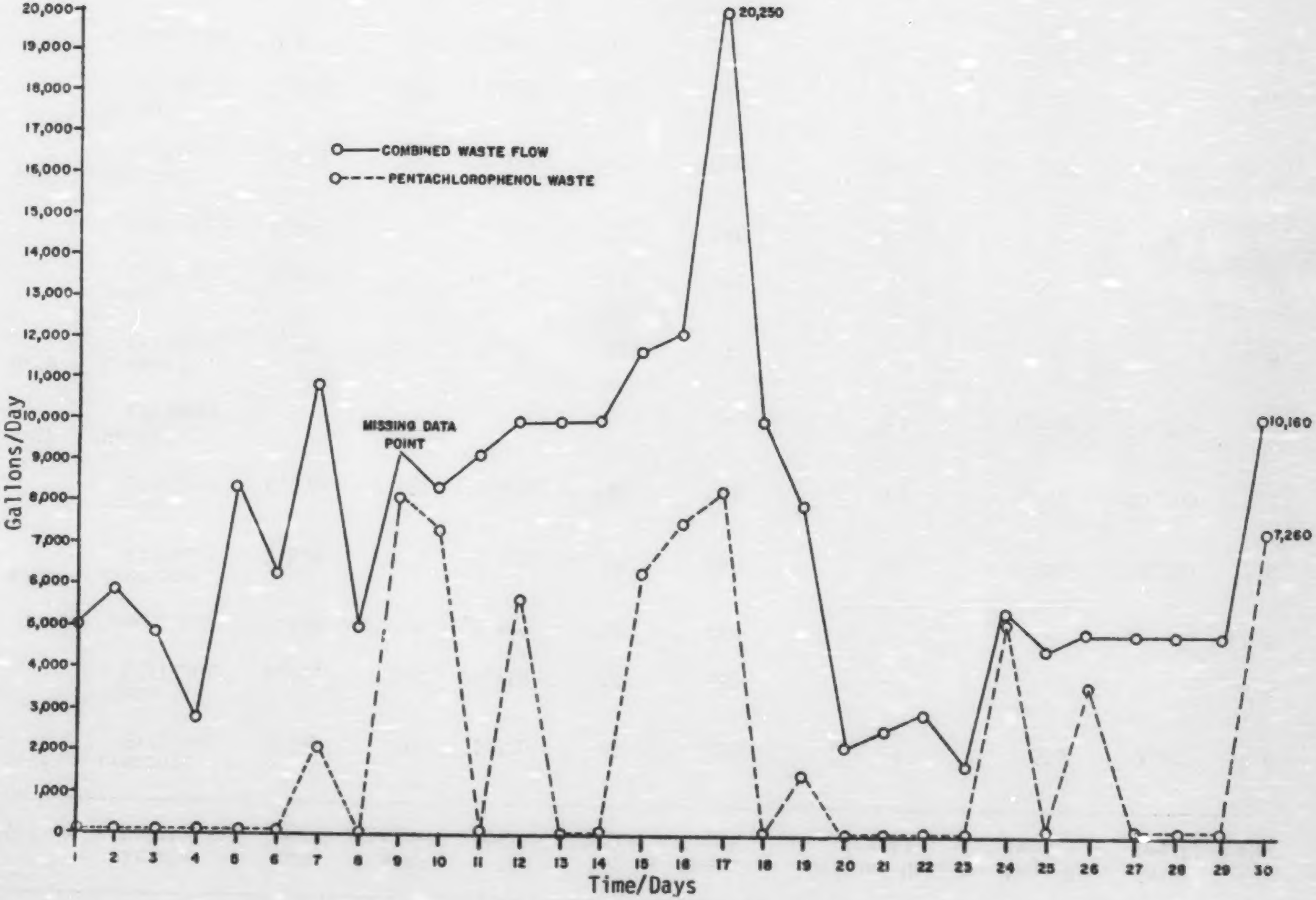

FIGURE 12. Flowrate Variation with Time

TABLE 14. Analytical Data From Pre-Design Study

Date	Sample Point	COD (mg/l)	BOD_5 (mg/l)	TS (mg/l)	TSS (mg/l)	Phenol (mg/l)	Oil and Grease (mg/l)	NH_3+-N (mg/l)	Total (mg/l)	pH
6-25	Creosote Effluent	2,130	615	4,270	147	100	89	550	3,200	5.6
	Penta Effluent	4,360	1,335	20,780	156	50	-	-	-	4.9
	Common Sump	2,130	600	5,480	181	120	-	-	-	5.6
6-26	Creosote Effluent	7,800	525	5,220	70	140	96	500	3,050	5.6
	Penta Effluent	6,900	1,395	19,830	138	65	178	1,750	10,200	4.7
6-27	Penta Effluent	-	-	-	-	-	263	1,650	11,200	-
6-28	Creosote Effluent	7,990	-	5,400	58	132	-	-	-	5.6
	Penta Effluent	4,720	-	19,980	143	70	-	-	-	4.9
	Common Sump	7,260	-	7,250	56	140	-	-	-	5.4
6-29	Creosote Effluent	3,209	1,200	4,184	142	200	275	500	2,050	5.7
	Penta Effluent	4,972	2,512	19,844	158	-	-	-	-	4.8
	Common Sump	2,621	-	4,447	174	-	-	-	-	5.7

TABLE 14. ANALYTICAL DATA FROM PRE-DESIGN STUDY

Date	Sample Point	COD (mg/l)	BOD_5 (mg/l)	TS (mg/l)	TSS (mg/l)	Phenol (mg/l)	Oil and Grease (mg/l)	NH_3+-N (mg/l)	Total (mg/l)	pH
	Average creosote effluent	5,282	780	4,769	104	143	153	517	2,767	5.6
	Penta Effluent	5,238	1,747	20,109	149	78	221	1,700	10,700	4.8
	Common Sump	4,004	600	5,726	137	130	-	-	-	5.6
	CALCULATED AVERAGE CONCENTRATIONS OF COMBINED EFFLUENTS	5,266	1,126	10,291	121	120	178	943	5,623	5.3

The ratio of BOD to COD for the calculated average data was relatively low, possibly indicating some degree of biological inhibition. Figure 13 shows the effluent dilution of the BOD test. When the dilution factor was increased from 99.6 to 99.9 percent, the BOD of the penta effluent increased from 1860 to 3500 mg/l. An increase in dilution from 99.8 to 99.9 percent for the creosote effluent resulted in a BOD increase from 1000 to 2000 mg/l. Assuming the samples were properly seeded, the value of the BOD test becomes questionable. While a limited amount of BOD data was collected during the study and is presented in this report where appropriate; the limitations on its usefulness should be noted in light of the above discussion.

The majority of the solids, as noted in Table 14, are composed of dissolved material which resulted for the most part from salts in fire retardant compounds which contained ammonium phosphate, ammonium sulfate, sodium tetraborate and boric acid as their primary constituents. Analyses performed later showed high boron levels. Also, the nutrient levels were relatively high due to the use of the fire retardant. The plant, subsequent to the pre-designed study, terminated the use of fire retardant preservative although boron persisted in the effluent for a period of time.

The phenol concentration averaged 120 mg/l during the study while the oil and grease concentration was 178 mg/l and pH averaged 5.3. No analytical data is given in Table 14 for penta because at the time of the pre-design study no suitable analysis technique had been developed. Later analyses by Koppers personnel indicated that the penta concentration was less than 20 mg/l.

DEVELOPMENT OF PARAMETERS

The average conditions determined in the pre-design study were chosen as the hydraulic basis for design. The average daily flow used for design was 27,063 lpd (7150 gpd) or 19 lpm (5 gpm). Further, it was decided that by maintaining Pond 2 as a surge lagoon it would be possible to operate the treatment facility at a constant feed rate and minimize the problems associated with flowrate and quality variations.

The pre-design data indicated that primary and secondary preservative recovery was efficiently removing most of the separable oils from the effluent. For this reason no modification of the existing oil removal system was considered necessary.

Laboratory studies by Thompson (46) and others indicated that biological oxidation of penta was possible. However, due to uncertainty with regard to the degree of reduction possible, the maximum concentration allowable, and the effects of penta on a biological system treating a complex, heterogeneous wastewater, it was decided that pretreatment with chlorine should be included in the design. Preliminary tests indicated that several hours detention time would reduce the chlorine residual to minimal levels. For this reason no chlorine removal facilities were included in the design of the pre-chlorination section of the treatment system.

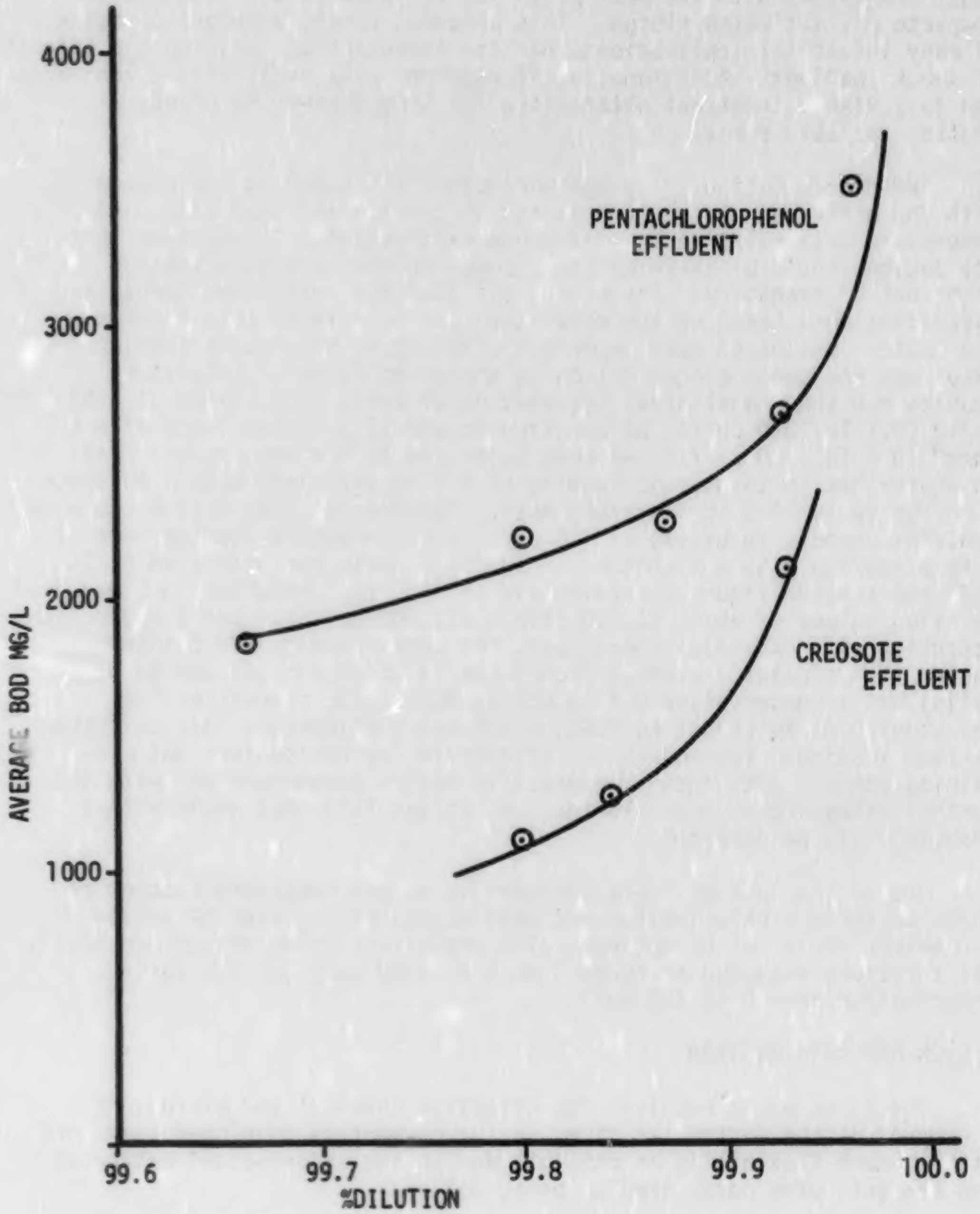

FIGURE 13.
Percent Dilution vs. BOD

On the basis of the limited information in the literature, recent laboratory data, and the consultant's experience with biological treatment, the system with the best potential for success was judged to be complete mix activated sludge. This process, having a record of success in many industrial applications, has the advantage of reducing the effects of shock loadings. Additionally, it requires relatively little land area and is a viable treatment alternative for wood preserving plants with little available space.

The determination of design parameters was based on experience with the activated sludge process and on the limited laboratory and literature data relative to wood preserving wastes. It was felt that the design should be based on the assumption that pre-chlorination might not be necessary. Therefore, all loadings, detention times, and capacities were based on the data shown in Table 14 of this section. The factor considered most important with regard to organic loading rates was the penta concentration in the mixed liquor. Laboratory results had shown biological degradation of penta at loadings of 1.62 gm/m^3 (0.1 lb/1000 cu ft) of aeration volume (71). Slug loads of 6.5 gm/m^3 (0.4 lb/1000 cu ft) had been tolerated in the same study. This is equivalent to an average loading of 4.2 kg penta/kkg MLSS with shock loadings up to 16.9 kg penta/kkg MLSS. Considering that this waste also contains phenols in excess of 100 mg/l, a conservative loading rate of 2 kg penta/kkg MLSS was chosen. Assuming a penta concentration of 20 mg/l and a mixed liquor concentration of 3000 mg/l resulted in a required aeration volume of about 83,270 liters (22,000 gallons) and a hydraulic detention time exceeding three days, the corresponding BOD loading (using the calculated average from Table 14 which was assumed to be valid) was a conservative 0.1 kg BOD/kg MLSS. The phenol loading rate was about 0.01 kg phenol/kg MLSS, which was considerably less that the maximum loadings recorded in the literature for wastewaters not containing penta. With these conservative design parameters and with the further safeguard of pre-chlorination, it was felt that satisfactory results could be obtained.

Due to the lack of field information on the necessary dosages of chlorine for pre-chlorination and post-chlorination, precise design parameters could not be defined. The pre-chlorination dosage capability was therefore designed to range from 0 to 4000 mg/l and the post-chlorination from 0 to 400 mg/l.

DESIGN AND CONSTRUCTION

The basic units required for effective chemical and biological treatment of the wastewater based on the parameters developed above and with as much flexibility as possible due to the experimental nature of the project, were considered to be as follows:

1. Surge or equalization basin. The existing Pond #2 was suitable for this purpose.
2. Influent pump. A small centrifugal pump with a maximum capacity of 37,850 lpd (10,000 gpd) mounted on a floating platform in Pond #2 was considered adequate.

3. Flow measurement and control device. The small flow could be easily measured with a rotameter and controlled with a valve.
4. Pre-chlorination unit. Total detention time equaling 12 hours with baffling for varying detention times and by-pass capability.
5. Aeration tank. A total volume of at least 83,290 lpd (22,000 gallons) should be divided into two or more sections for varying loading rates.
6. Final clarifier. An overflow rate of 8150 to 12,200 lpd/m^2 (200 to 300 gpd/ft^2) was considered necessary.
7. Post chlorination tank. A detention time of 8 to 10 hours was provided.
8. Chlorine injector equipment. A variable feed rate up to 91 kg/day (200 lb/day) was provided.
9. Aerobic digester. A retention period of 15 to 20 days was allowed.
10. Final sludge disposal was to be by irrigation on an existing field.

A package unit was delivered by Davco in January 1973. As illustrated in Figure 14, the treatment plant consisted of two rectangular tanks and a separate circular clarifier. The first rectangular tank, 3.66 m (12 ft) wide by 9.75 m (32 ft) long, was divided into an aerobic digestion tank and pre-chlorination tank, each approximately 1.83 m (6 ft) in length, and the #1 aeration tank which was about 6.1 m (20 ft) long. The second tank was 2.44 (8 ft) wide by 11.6 m (38 ft) long and was divided into two sections, the #2 aeration tank which was about 7.9 m (26 ft) long, and the post chlorination tank which was about 1.83 m (6 ft) long. The clarifier had a diameter of approximately 2.44 m (8 ft). Flow entered either the pre-chlorination chamber or moved directly to the aeration tank. At 19 lpm (5 gpm), the detention time in the pre-chlorination tank was about 15 hours. This tank was later baffled to provide variable detention times. The aeration time in the #1 tank was about 50 hours. All activated sludge was returned to this tank. The flow then entered aeration tank #2 which had a detention time of 47 hours at a flow of 19 lpm (5 gpm). The mixed liquor from tank #2 then settled in the clarifier which had a surface overflow rate of less than 6100 lpd/sq m 150 gpd/sq ft) at the average design flow of 27,250 lpd (7200 gpd). The clarifier overflow could be post chlorinated prior to final discharge.

Air was supplied to the aeration tanks, aerobic digester, and the air lift sludge return line by a duplex blower driven by a 7.5 hp motor. The total expected air requirement was 5.2 cu m/min at 1.34 atm (185 cfm at 5 psig).

The entire plant was placed on a reinforced concrete slab above ground. All extension surfaces were coated with insulating material to protect against severe winter weather. Heater tape was placed on exposed pipes and valves and electric immersion heaters were placed in the aeration tanks.

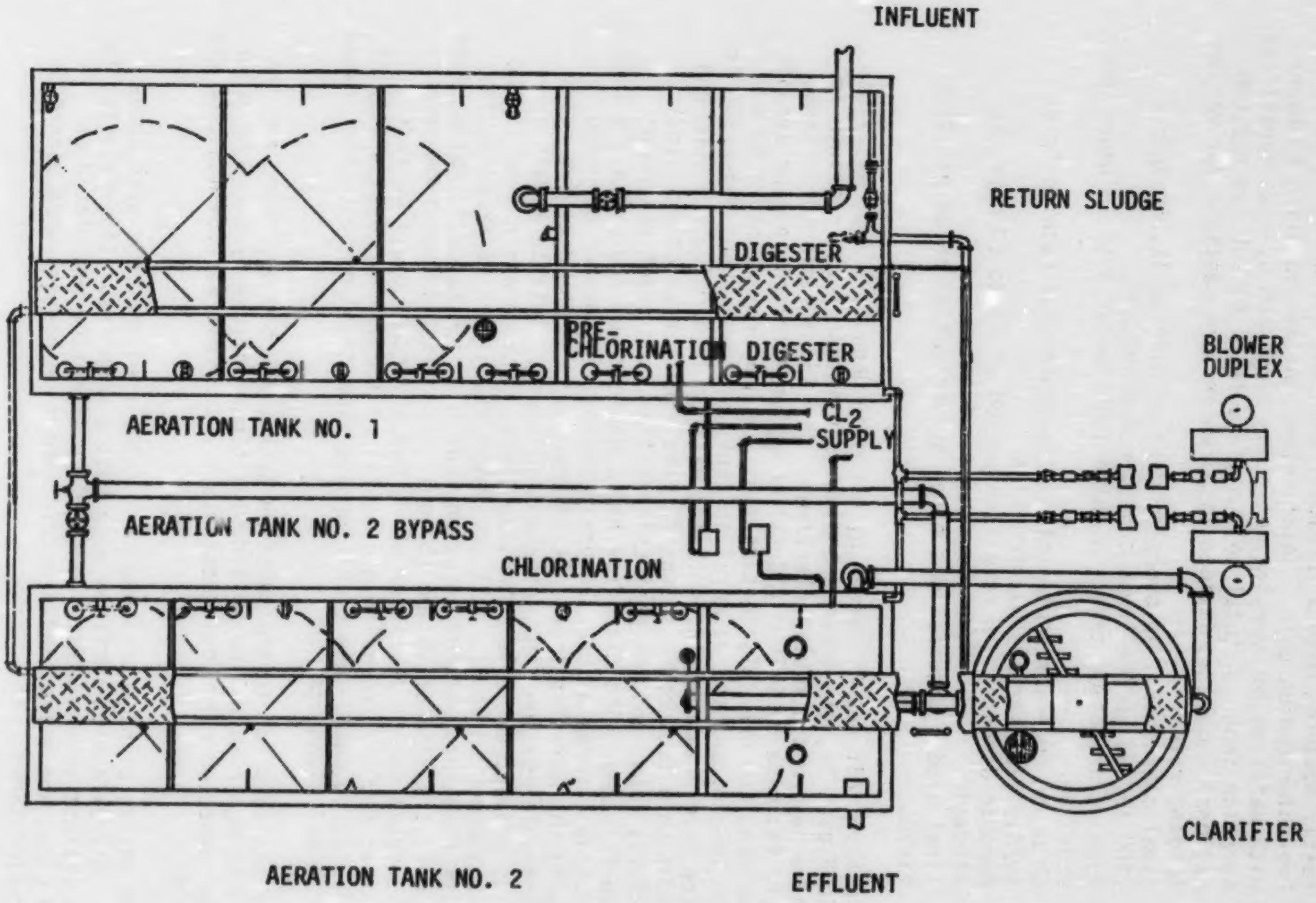
INFLUENT
RETURN SLUDGE
DIGESTER
PRE-CHLORINATION
DIGESTER
BLOWER DUPLEX
CL2 SUPPLY
AERATION TANK NO. 1
AERATION TANK NO. 2 BYPASS
CHLORINATION
CLARIFIER
AERATION TANK NO. 2
EFFLUENT

FIGURE 14.
Schematic of "Package" Treatment System

Due to the high nutrient levels observed in the pre-design study, no nutrient addition was provided in the final design. Control of pH, was not included in the final design. It was found that manual addition of lime to the aeration basins on an as needed basis would provide satisfactory pH control.

In addition to the treatment plant itself, laboratory facilities were also constructed on-site. A full time chemist was employed to perform all analyses on-site with the exception of BOD tests which were conducted by an outside laboratory. A treatment plant operator was trained to maintain and operate the plant and also to assist in performing daily sample collections and analyses.

PLAN OF OPERATION

The original operating schedule developed for the project was based on the uncertainty of the effects of pentachlorophenol on the activated sludge process. The original schedule is as follows:

Month #1 - Chlorinate the effluent at 100 percent of chlorinator capacity using full detention time in prechlorination facility. With BOD loading equaling 0.1 kg BOD/day/kg MLSS, maintain MLSS around 3,000 mg/l. Post-chlorinate to produce an effluent phenol concentration of 0.1 mg/l.
Month #2 - Reduce pre-chlorination to 50% of capacity or chlorinate only half of the influent stream at 100% capacity, otherwise, maintain steady-state conditions.
Month #3 - Reduce pre-chlorination by 50% again, resulting in a total decrease since initial operation of 75%. Maintain constant conditions.
Month #4 - Based on the previous three months of operation, discontinue pre-chlorination entirely or operate at the miniumum level apparently required. Determine this level by examining the condition of the biological process during the first three months. Also, study the effect of detention time on chlorination by collecting samples from each section of the baffled pre-chlorination tank.
Month #5 - Maintain pre-chlorination at the minimum level determined above or increase it as necessary while doubling BOD and PCP loadings by halving the aeration tank volume. Also, attempt a 20% reduction in MLSS concentration.
Month #6 - Pre-chlorinate as necessary while again reducing MLSS by 20%. After two weeks, if possible, reduce MLSS by another 20%.
Month #7 - Pre-chlorinate as necessary while again reducing MLSS by 20% with further reductions if possible.
Month #8 - Operate at steady state conditions utilizing the optimum pre- and post- chlorination dosages determined during the operating period, as well as the corresponding optimum BOD and penta loading rates.

Although the package plant arrived in Carbondale in February 1973, because of inclement weather it was not ready for startup until July.

Due to the delay, it was decided to initiate operation without pre-chlorination and thereby determine immediately whether chlorination would be required.

On this basis, plant startup procedures were initiated on July 26, 1973. The aeration basins were filled with water from the emergency lagoon, Pond #1, which had low concentrations of boron, phenols, and penta. Bacterial inoculation was accomplished by placing horse manure into the aeration tank and aeration was begun. One week later a 23 lpm (6 gpm) feed mixture of emergency lagoon water and concentrated waste from Pond #2 was begun. By the middle of August the proportion of the mixture consisting of concentrated waste had been increased to 100 percent. Normal mechanical problems were encountered during the initial startup period. During the latter part of August, a pin sheared in the clarifier sludge rake mechanism and one pump failed. The sludge rake malfunction resulted in low MLSS concentrations throughout August. After the shear pin was replaced, the treatment plant was again placed in operation and startup was continued through September 1973.

Because of the immediate success of the complete mix process without pre-chlorination, the entire operating schedule was modified. This revised schedule is shown in Table 15. Due to inclement weather and later mechanical failures, this schedule could not be adhered to exactly; however, all the desired objectives were accomplished during the study period.

TESTING SCHEDULE

The on-site laboratory was equipped with the necessary materials to perform basic gravimetric, colorimetric, and titrametric analyses including COD, solids, nutrients, phenols, pentachlorophenol, oil and grease, residual chlorine, pH, temperature, and dissolved oxygen. BOD analyses were performed by an outside laboratory and any special analyses required such as gas chromatography or metal analyses were performed elsewhere.

Samples were collected daily for analysis. Batch samples were used instead of composites because of the presence of the large surge lagoon which minimized fluctuations and because of the large detention time in the treatment plant itself which tended to smooth out variations throughout the system.

Due to the large number of analyses needed and the limited staff at Carbondale, a schedule of analyses based on the minimum requirements for experimentation and the manpower limitations had to be developed. The schedule shown in Table 16 was followed throughout the study period. During periods when more information was desired in one unit of the treatment system than another, more analyses were performed. For instance, when the effects of post-chlorination were being closely studied, more chlorine residual determinations were required. BOD, COD, phenol, solids, and oil and grease analyses were performed according to Standard Methods (13 edition) (72). Nutrients were analyzed

TABLE 15. REVISED OPERATING SCHEDULE

Month	Objective	Operation
# 1	Startup and shakedown	Inoculate aeration tanks with activated sludge or other bacteria source. Operate plant with increasing proportion of concentrated waste and decreasing proportion of dilution water. Shakedown mechanical equipment, repairing and replacing as necessary.
# 2	Hydraulic loading variation	Increase the hydraulic loading to the treatment system in increments up to the limit of hydraulic capacity or organic loading rate, whichever is reached first.
# 3	Organic loading variation	Restabilize the process at 4 to 6 gpm using only one aeration basin.
# 4	Increased organic loading	Reduce the mixed liquor suspended solids or increase the flow rate incrementally.
# 5	Increased organic loading	Continue reducing the MLSS or increasing the flow rate incrementally.
# 6	Post-chlorination studies	Measure the effects of post-chlorination on PCP, phenol, COD and BOD concentrations at various dosages, increasing the dosage incrementally over the month.
# 7	Pre-chlorination studies	Operate the treatment plant at near constant conditions while increasing the pre-chlorination dosage incrementally and measuring its effect on the activated sludge process.
# 8	Optimization	Based on the previous months' experience, operate the process at those conditions which gave the best results including pre- and post-chlorination as necessary.

TABLE 16. SCHEDULE OF ANALYSES

	Sampling Point and Number of Analyses Per Week				
Parameter	Influent	Prechlorination	Aeration Basins	Clarifier	Post Chlorination
BOD	2	1	2	1	2
COD	2	1	2	1	2
Phenol	2	1	2	1	2
Penta	2	1	2	1	2
TS	2	-	-	-	2
TSS	2	-	3	-	2
VSS	-	-	3	-	-
TDS	2	-	-	-	2
NH_4+	1	-	-	-	1
PO_4=	1	-	-	-	1
SVI	-	-	2	-	-
Oil and grease	1	-	-	-	1
Temperature	-	-	5	-	-
D.O.	-	-	5	-	-
pH	5	-	5	-	-
Cl_2 Residual	-	0-5	-	-	0-5

with colorimetric kits. The determination of penta proved to be difficult and, in fact, no truly satisfactory method was found. The method chosen at the beginning of the study after careful evaluation of the two or three methods available was the Safranin method which is a distillation and color development technique.

SECTION VI

RESULTS AND DISCUSSION

The experimentation phase of the project was begun in July 1973, and was completed in May 1974. The raw data collected during the study is contained in the Appendix.

PHASE 1 - START-UP AND STABILIZATION

The start-up of the treatment system was accomplished with relatively little difficulty. Without the mechanical start-up problems encountered, the activated sludge process could have been stabilized in two weeks, but, with the mechanical problems, as previously discussed, the start-up and stabilization phase took about five weeks. A significant amount of data was not collected during the start-up period; however, most of the data obtained is presented in Table 17. The average influent and effluent concentrations of COD for the five week period were 1540 mg/l and 410 mg/l, respectively, which is a reduction efficiency of 73 percent. The phenol reduction efficiency for the same period was 97 percent. The influent penta concentration was much less than expected but a reduction through the treatment system of 79 percent was obtained.

PHASE 2 - STEADY STATE OPERATION

For a period of about four weeks (August 30 through October 5, 1973), the treatment plant was operated at constant flow and loading to evaluate the performance of the activated sludge process under controlled conditions. During this phase, flowrate was maintained at 23 liters per minute (six gallons per minute), and influent COD averaged 178 mg/l, influent phenols averaged 88 mg/l, and influent penta averaged 1.7 mg/l. The average results of this period are presented in Table 18 and, as can be seen, the effluent quality varied little during the four week period indicating a stable biological process. Effluent COD averaged 404 mg/l and never varied more than 10 percent from this value. Effluent phenols rarely varied from the average value of 1 mg/l. The effluent PCP value never exceeded 0.6 mg/l and averaged 0.4 mg/l. As it turned out, the loading rate was not constant because of sludge buildup. However, in general, it can be concluded from this data that a conservatively designed activated sludge process treating creosote and pentachlorophenol wastewater should be able to reduce COD by 75 to 80 percent, phenols by 95 to 99 percent, and PCP by 75 to 80 percent.

PHASE 3 - LOADING RATE VARIATION

Phase 2, Steady-State Operation, was terminated after the first week in October 1973. From that time until mid-November, experimentation was directed primarily at examining the effects of loading rate variations on the activated sludge process. Due to the conservative design of the treatment system, a considerable degree of variation both in organic and hydraulic loading rate was possible.

TABLE 17. STARTUP AND STABILIZATION DATA

	Flow, liters per minute			Parameter			
Date 1973	Dilution Water	Concentrated Waste	Sampling Point	COD (mg/l)	Phenols (mg/l)	PCP (mg/l)	Sludge (ml/l)
7-30	0	0	#1 Aeration	-	1	-	0
			Dilution	-	1	-	-
			Raw Waste	-	150	-	-
7-31	0	11,350	#1 Aeration	-	16	-	-
			#2 Aeration	-	8	-	-
			Effluent	-	5	-	-
8-1	0	0	#1 Aeration	-	1	0.6	-
			#2 Aeration	-	1	0.6	-
			Effluent	-	1	0.6	-
8-2	0	0	#1 Aeration	-	0.6	-	0.2
			#2 Aeration	-	0.6	-	0.3
			Effluent	-	0.6	-	-
8-3	17.0	1.89	Influent	-	1	-	-
			#1 Aeration	-	1	-	0.1
			#2 Aeration	-	1	-	0.05
			Effluent	-	1	-	-
8-4	15.1	3.8	Influent	-	10	-	-
			Effluent	-	1	-	-
8-5	13.2	5.7	Influent	-	12	-	-
			Effluent	-	1	-	-
8-6	11.4	7.6	Influent	-	15	-	-
			#1 Aeration	-	1	-	0.1
			#2 Aeration	-	1	-	0.1
			Effluent	-	1	-	-
8-8	3.8	15.1	Influent	-	30	-	-
			#1 Aeration	-	1	-	0.1
			#2 Aeration	-	1	-	0.1
			Effluent	-	1	-	-
8-10	3.8	15.1	Influent	-	65	-	-
			#1 Aeration	-	1.5	-	0.3
			#2 Aeration	-	1.6	-	0.4
			Effluent	-	1.4	-	-

TABLE 17. STARTUP AND STABILIZATION DATA

Date 1973	Flow, liters per minute: Dilution Water	Flow, liters per minute: Concentrated Waste	Sampling Point	Parameter: COD (mg/l)	Parameter: Phenols (mg/l)	Parameter: PCP (mg/l)	Parameter: Sludge (ml/l)
8-16	3.8	15.1	Influent	-	70	-	-
			#1 Aeration	-	2	-	0.7
			#2 Aeration	-	2	-	0.6
			Effluent	-	2	-	-
8-17	1.9	15.1	Influent	-	70	-	-
			#1 Aeration	-	3	-	0.5
			#2 Aeration	-	2	-	0.4
			Effluent	-	2	-	-
8-20	0	11.4	Influent	-	70	-	-
	(Pump Problems)		Effluent	-	1	-	-
8-21	0	7.6	Influent	1,260	70	3.4	-
			#1 Aeration	-	1.5	-	0.4
			#2 Aeration	-	1.5	-	0.4
			Effluent	350	1.5	0.6	-
8-23	0	11.4	Influent	-	70	3.4	-
	(Pumps Required)		Effluent	-	1.5	0.3	-
8-24	0	15.1	Influent	-	70	2.6	-
			Effluent	-	1	0.3	-
8-27	0	22.7	Influent	-	80	-	-
			#1 Aeration	-	3	-	2.0
			#2 Aeration	-	2	-	1.7
			Effluent	-	2	-	-
8-28	Clarifier paddles found to be not functioning						
8-29	Clarifier paddles repaired						
8-30	0	22.7	Influent	1,820	85	3.0	-
			#1 Aeration	-	3	-	11.0
			#2 Aeration	-	2	-	7.5
			Effluent	470	2	0.7	-
8-31	0	22.7	Influent	-	95	-	-
			#1 Aeration	-	3	-	13.0
			#2 Aeration	-	2	-	9.5
			Effluent	-	2	-	-

TABLE 17. STARTUP AND STABILIZATION DATA

Date 1973	Flow, liters per minute Dilution Water	Flow, liters per minute Concentrated Waste	Sampling Point	Parameter COD (mg/l)	Parameter Phenols (mg/l	Parameter PCP (mg/l)	Parameter Sludge (ml/l)
AVERAGE OF ALL STARTUP PERIOD DATA			Influent	1,540	56	2.9	34
			#1 Aeration	-	2	-	30
			#2 Aeration	-	2	-	-
			Effluent	410	2	0.6	43
				PO_4	NH_4^+		
			Influent	-	-		
			#1 Aeration	555	47.5		
			#2 Aeration	430	56.7		
			Effluent	440	66.0		

TABLE 18. EFFECTS OF SHOCK LOADING

Average Values from Steady State Operation - mg/l

Flow Rate		COD	Phenols	PCP
	Influent	1784	88	1.7
22.7 lpm (6 gpm)	Effluent	404	1	0.4
	Reduction	77%	99%	76%

Result of Shock Loading

Flow Rate		COD	Phenols	PCP
41.6 lpm (11 gpm)	Influent	2650	90	1.62
	Effluent	710	10	1.32
	Reduction	73%	88%	19%

The effects of shock loading were observed during a three day period. The flowrate, which had been maintained at a constant 21 liters per minute (5.5 gpm) for over four weeks, was increased to 42 lpm (11 gpm) on October 8 and maintained at this rate for three days. At this rate, the nominal detention time in the aeration tanks was 44 hours, the BOD: MLSS ratio was about 0.13 kg BOD/kg MLSS, and the COD:MLSS ratio exceeded 0.5 kg COD/kg MLSS. The penta loading was below 1 gm/cu m (0.06 lb per 1000 cu ft) of aeration volume. While this is still far below the shock loadings of Thompson (46) -- 6.5 gm/cu m (0.4 lb per 1000 cu ft), the detention time was less than one-half of the five day detention used in his laboratory studies. The result of this increased loading and decreased detention time was a noticeable decrease in treatment efficiency as shown in Table 18. Phenol concentration increased rapidly in both aeration tanks as well as in the effluent. Phenol removal efficiency decreased from 99 percent to about 89 percent and was decreasing rapidly with time. COD removal efficiency was less affected but did show a decrease in efficiency from near 80 percent to about 72 percent. BOD removal was apparently not affected but, as noted previously, the value of the BOD test for this waste is questionable. It is noteworthy that penta removal efficiency was apparently affected by the shock loading. At a constant loading, the penta removal had averaged 79 percent but, apparently because of the shock loading, this was reduced to virtually zero removal of penta. Whether the decreased removal efficiency was due to a decrease in the rate of oxidation of penta or to the decreased hydraulic detention time was not determined.

In order to determine the effects of increased loading and decreased detention time under more constant conditions, two series of loading variation were initiated. The flowrate was increased incrementally from 20.8 lpm (5.5 gpm) to a maximum of 41.6 l pm (11 gpm) for the first series and to a maximum of 49 l pm (13 gpm) for the second series. The first series of incremental flow variation was conducted during the last two weeks of October and the second series during the first two weeks of November.

The activated sludge process was restabilized for a four day period after the shock loading test. On October 15, the flow rate was increased to 26.5 lpm (7 gpm), then 34 lpm (9 gpm) on the 16th, and finally to 41.6 lpm (11 gpm) by the 18th of October. The flowrate was maintained at 41.6 lpm (11 gpm) for about one week. The results of this phase of experimentation are shown in Table 19. As the loading was increased, the penta removal efficiency again decreased until virtually no removal was obtained.

The phenol removal efficiency decreased slightly but the effluent concentration of phenol never exceeded 3.0 mg/l. Apparently, as the loading was increased, the capacity of the activated sludge in the first aeration basin to oxidize phenols was approached and exceeded. As the loading was increased the concentration of phenols in the first aeration tank increased. This resulted in an increase in the loading on the second tank and some increase in effluent phenol concentration. The increased loading on the second aeration tank produced a rapid buildup of suspended solids which indicated increased biological activity.

TABLE 19. RESULTS OF LOADING RATE VARIATION

Date 1973	Flow lpm	Sampling Point	COD (mg/l)	BOD (mg/l)	Phenol (mg/l)	PCP (mg/l)	Sludge (ml/l)
(FIRST LOADING SERIES)							
10-15	26.5	Influent	-	-	75	2.15	-
		#1 Aeration	-	-	2	-	400
		#2 Aeration	-	-	1	-	305
		Effluent	-	-	1	1.62	-
10-16	35.1	Influent	-	-	75	-	-
		#1 Aeration	-	-	3	-	430
		#2 Aeration	-	-	2	-	330
		Effluent	-	-	1	-	-
10-17	35.1	Influent	2117	-	80	-	-
		#1 Aeration	-	-	3	-	470
		#2 Aeration	-	-	2	-	340
		Effluent	757	-	1	-	-
10-18	41.6	Influent	-	-	90	2.15	-
		#1 Aeration	-	-	5	-	500
		#2 Aeration	-	-	3	-	365
		Effluent	-	-	2	2.15	-
10-19	41.6	Influent	-	755	75	2.28	-
		#1 Aeration	-	-	5	-	500
		#2 Aeration	-	-	2	-	380
		Effluent	-	75	1	1.78	-
10-24	41.6	Influent	2117	-	70	-	-
		#1 Aeration	-	-	6	-	560
		#2 Aeration	-	-	4	-	440
		Effluent	846	-	3	-	-
(SECOND LOADING SERIES)							
11-2	20.8	Influent	-	1045	90	2.3	-
		#1 Aeration	-	-	3	-	600
		#2 Aeration	-	-	2	-	425
		Effluent	-	110	1	2.4	-
11-6	20.8	Influent	2290	-	90	-	-
		#1 Aeration	-	-	3	-	680
		#2 Aeration	-	-	2	-	490
		Effluent	730	-	1	-	-

TABLE 19. RESULTS OF LOADING RATE VARIATION

Date 1973	Flow lpm	Sampling Point	Parameter				
(FIRST LOADING SERIES)			COD (mg/l)	BOD (mg/l)	Phenol (mg/l)	PCP (mg/l)	Sludge (ml/l)
11-7	26.5	Influent	-	-	90	2.1	-
		#1 Aeration	-	-	5	-	700
		#2 Aeration	-	-	3	-	470
		Effluent	-	-	2	2.1	-
11-8	36.0	Influent	-	-	100	-	-
		#1 Aeration	-	-	5	-	620
		#2 Aeration	-	-	2	-	470
		Effluent	-	-	1	-	-
11-9	41.6	Influent	-	-	90	2.4	-
		#1 Aeration	-	-	7	-	690
		#2 Aeration	-	-	3	-	480
		Effluent	-	-	2	2.2	-
11-12	49.2	Influent	-	-	80	2.7	-
		#1 Aeration	-	-	9	-	-
		#2 Aeration	-	-	5	-	-
		Effluent	-	-	2	3.2	-
11-13	49.2	Influent	2650	-	90	-	-
		#1 Aeration	-	-	25	-	525
		#2 Aeration	-	-	15	-	580
		Effluent	1040	-	10	-	-
11-14	49.2	Influent	-	-	90	3.1	-
		#1 Aeration	-	-	25	-	500
		#2 Aeration	-	-	20	-	500
		Effluent	-	-	20	2.7	-
11-15	0	Effluent	-	-	40	-	-

(Flowrate Variation Discontinued)

The COD removal efficiency, which had decreased during the earlier period of shock loading, continued to decrease during this period also. By October 24, the COD removal efficiency had decreased to about 60 percent. During the same period, however, BOD analyses indicated good BOD removal efficiency. On October 19, with the flowrate at 41.6 lpm (11 gpm), the BOD removal was 93 percent.

The second series of loading variation was begun on November 7, following a week-long period of stabilization at the design flowrate. The flowrate was increased to 49 lpm (13 gpm) over a five day period, the results of which are shown in Table 19. The results are quite similar to those obtained in the October series of loading variation. Virtually no penta removal occurred and the COD removal efficiency was reduced to about 60 percent. The buildup of phenol in both aeration basins occurred as before. However, at 49 lpm (13 gpm) the oxidation of phenols decreased very rapidly and was accompanied by sludge bulking in the clarifier. At this rate, detention time in the aeration tanks was 37 hours, the BOD:MLSS ratio was approximately 0.12 kg BOD/day/kg MLSS and the COD:MLSS ratio equalled 0.36 kg COD/day/kg MLSS. The penta loading was nearly 1.8 gm/cu m (0.11 lb/1000 cu ft) of aeration volume and the phenol:MLSS ratio was 0.01 kg phenol/day/kg MLSS.

Because of the fact that the hydraulic capacity of the treatment system was probably exceeded at 49 lpm (13 gpm) and because the detention time in the aeration basins was less than 50 percent of the design aeration time, the above loadings probably do not represent the maximum organic loading conditions at which the complete mix activated sludge process could effectively function. It was therefore decided to reduce the aeration volume by about 50 percent by utilizing only one aeration tank. By then increasing the flowrate or decreasing the MLSS, a comparatively large change in loading could be obtained without hydraulically overloading any unit of the treatment system. Before this phase of the experimentation could be commenced, however, severe winter weather including snow, ice, and subzero temperatures set in. At the same time, the immersion heaters which had been placed in the aeration tanks failed. The result was a period from December 8, 1973, through January 17, 1974, during which the treatment plant was inoperative due to frozen and broken valves and pipes. During this period the aeration tank contents were aerated to maintain aerobic conditions. Following a period of a few warm days in mid-January, the necessary repairs were completed and plant operations resumed.

It should be noted that the activated sludge responded immediately to the reintroduction of feed water and stability was soon apparent.

As noted above, it had been decided to utilize only one aeration tank for the purpose of loading variation. Because of the continuing cold weather, it was decided to postpone further loading variation until spring. The main experimentation efforts for the period from January 17, 1974, through March 4, 1974, were directed at observing the effects of post-chlorination of effluent quality. In order to maintain continuity, this period will be discussed out of chronological order so that the results of loading variation can be concluded.

Loading variation recommenced on March 5, 1974, following the post-chlorination study. As mentioned previously, this portion of the study was performed using only the first aeration basin which had a volume of about 56,400 liters (14,900 gallons). The initial flowrate was 15 lpm (4 gpm) and the detention time in the aeration tank was 62 hours. The BOD:MLSS ratio was approximately 0.10 kg BOD/day/kg MLSS, the COD:MLSS ratio was 0.27 kg COD/day/kg MLSS, the ratio of phenol to MLSS equalled 0.007 phenol/day/kg MLSS, and the penta loading reached 3.2 gm/cu m (0.2 lb/1000 cu ft) of aeration volume. Using this configuration of treatment units at 15 lpm (4 gpm), a COD reduction of 70 percent, a BOD reduction of 85 percent, and a phenol reduction of 99 percent were obtained.

From March 4 through the end of April the flowrate was increased in increments from 15 lpm to 30 lpm (4gpm to 8 gpm). At first, it appeared that a flowrate of 19 to 23 lpm (5 to 6 gpm) was the maximum rate which could be handled without upsetting the biological process. As can be seen in Figure 15, on three different occasions as this flowrate was reached, the phenolic reduction decreased rapidly. The sludge settling characteristics also changed at this loading with the sludge volume index (SVI) increasing from about 100 to over 200. On the third occasion the flowrate was increased beyond this loading range to a maximum of 30 lpm (8 gpm). At this loading, the activated sludge appeared to restabilize considerably and the SVI decreased to approximately 100. The phenol reduction efficiency again returned to 99 percent removal and BOD was removed at about 90 percent efficiency. COD removal had decreased markedly at this loading, however, to about 57 percent. Also, the plant operator reported that after about five days at 30 lpm (8 gpm), sludge was beginning to rise in the clarifier. At this point loading variation was suspended. Thus, the maximum loadings achieved with a 31 hour detention time were a COD:MLSS ratio of 0.50 kg COD/day/kg MLSS, a BOD:MLSS ratio of 0.18 kg BOD/day/kg MLSS, a phenol:MLSS ratio of 0.013 kg phenol/day/kg MLSS, and a penta loading of 7.3 gm/cu m (0.45 lb penta/1000 cu ft) of aeration volume. As can be seen, these are relatively high loading rates. The detention time of 31 hours is much less than that reported for penta removal and the penta loading exceeds the maximum loading attempted in previous laboratory studies.

PHASE 4 - POST-CHLORINATION STUDIES

Post-chlorination studies were begun on February 6, 1974, with the primary objective of determining the effects of chlorine on effluent quality. During this period of the study, the activated sludge process was operated with one aeration basin. The influent flowrate was maintained at 15 lpm (4 gpm) and the MLSS concentration was held constant at about 3500 mg/l by wasting sludge as necessary. All other operating parameters were maintained constant to minimize as many variables as possible during the post-chlorination phase of the study.

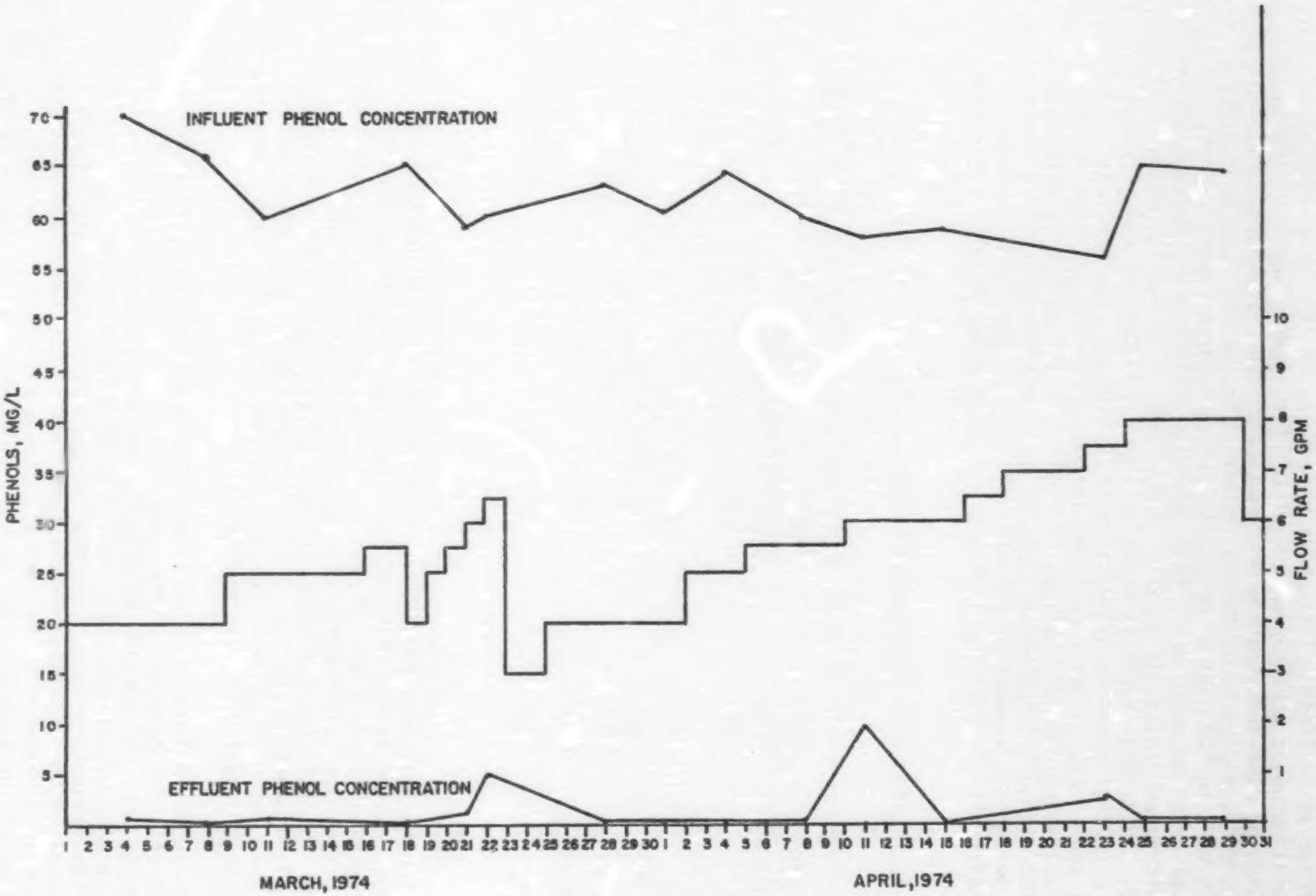

FIGURE 15.
Influent and Effluent Phenol Concentration

Prior to initiating full-scale post-chlorination, some laboratory scale studies were performed on the clarified effluent to determine the range of post-chlorination which would be most effective. For this purpose, sodium hypochlorite (clorox) was used at dosages ranging from 15 mg/l to 500 mg/l as HOCl. As illustrated in Figure 16, the residual chlorine stabilized within thirty minutes for all dosages and then decreased slowly, if at all. The effect of increasing dosage on COD, penta, and phenol is shown in Table 20. Minimal reduction in COD occurred at even the 500 mg/l chlorine dosage. The effluent phenol was already below 1 mg/l and the reduction due to chlorine was not significant. As can be seen in Figure 17, the effect of chlorine on penta was quite significant, producing a maximum apparent reduction of 77 percent at a chlorine dosage of 250 mg/l. The normally brown wastewater was considerably lightened in color with increasing chlorine dose.

TABLE 20. LABORATORY POST-CHLORINATION STUDIES

Cl_2 Dosage (mg/l)	Time (min)	Penta	Phenol	COD
		(percent reduction)		
15	40	16	--	--
30	40	31	--	--
45	40	38	--	--
250	60	77	25	7
500	60	75	33	12

In spite of the lack of beneficial results from the laboratory study, full-scale post-chlorination studies were conducted to confirm the laboratory results and to further study the effects of chlorine on penta. Chlorine was injected into the post-chlorination tank at concentrations varying from 7 mg/l to 155 mg/l as HOCl. The detention time in the post-chlorination tank at 15 lpm (4 gpm) was about 10 hours. The MLSS concentration was maintained between 3500 and 4000 mg/l. The immersion heaters in the aeration tank limited temperature variations while pH was held constant by lime additions. The dissolved oxygen concentration was maintained at 2 mg/l.

As shown in Table 21, there was no reduction in COD even at the highest chlorine dosage. Phenol concentrations in the effluent were reduced by about 50 percent at chlorine residuals exceeding 11.1 mg/l. There were apparent reductions in BOD ranging up to 64 percent. However, the validity of this reduction is questionable considering the retardance of the BOD test and the fact that no COD reduction occurred. The effect of chlorine on penta was either a reduction of penta or a reduction of the concentration of substances which interfered with the analysis for penta.

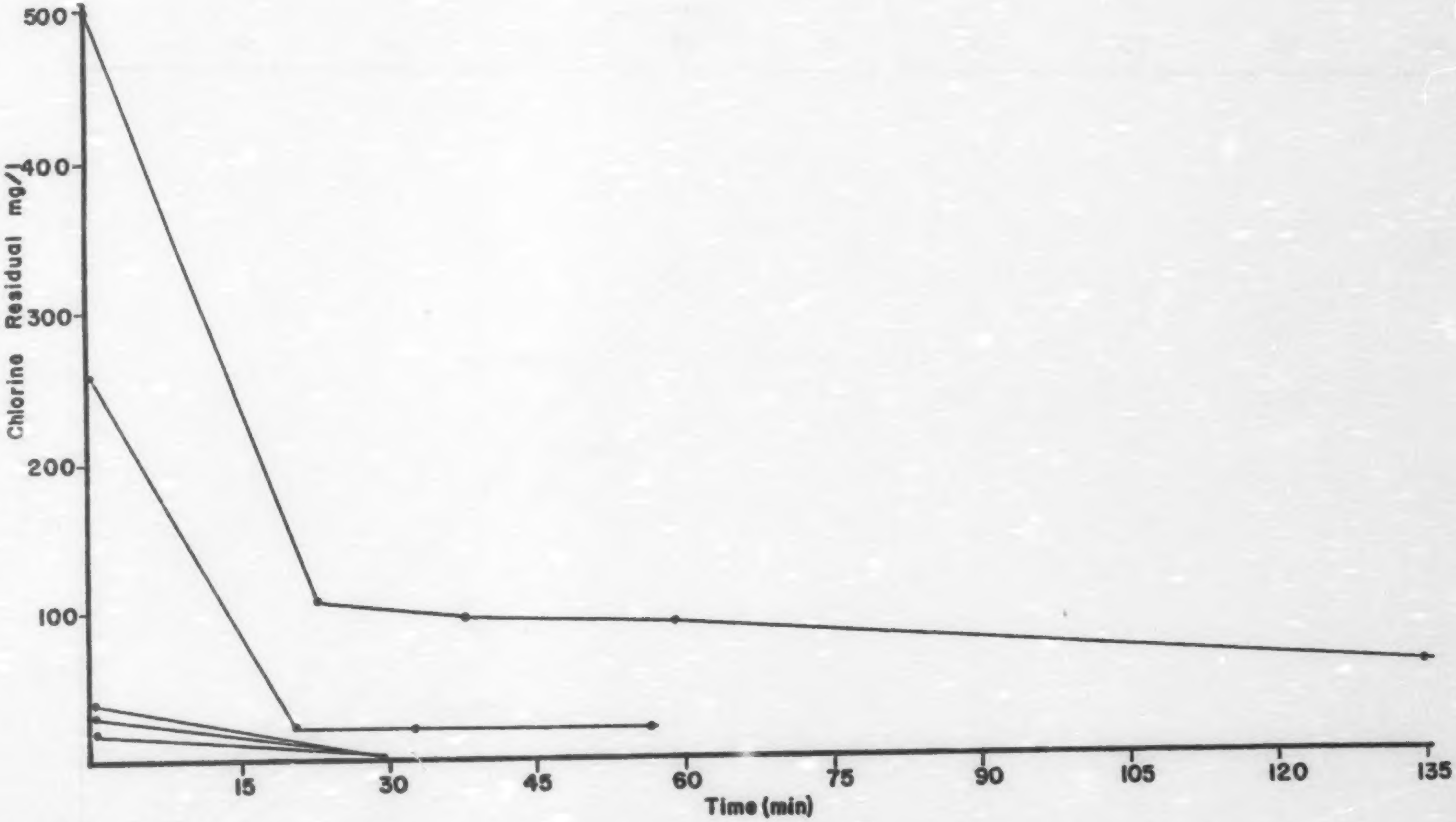

FIGURE 16.
Chlorine Residuals with Time

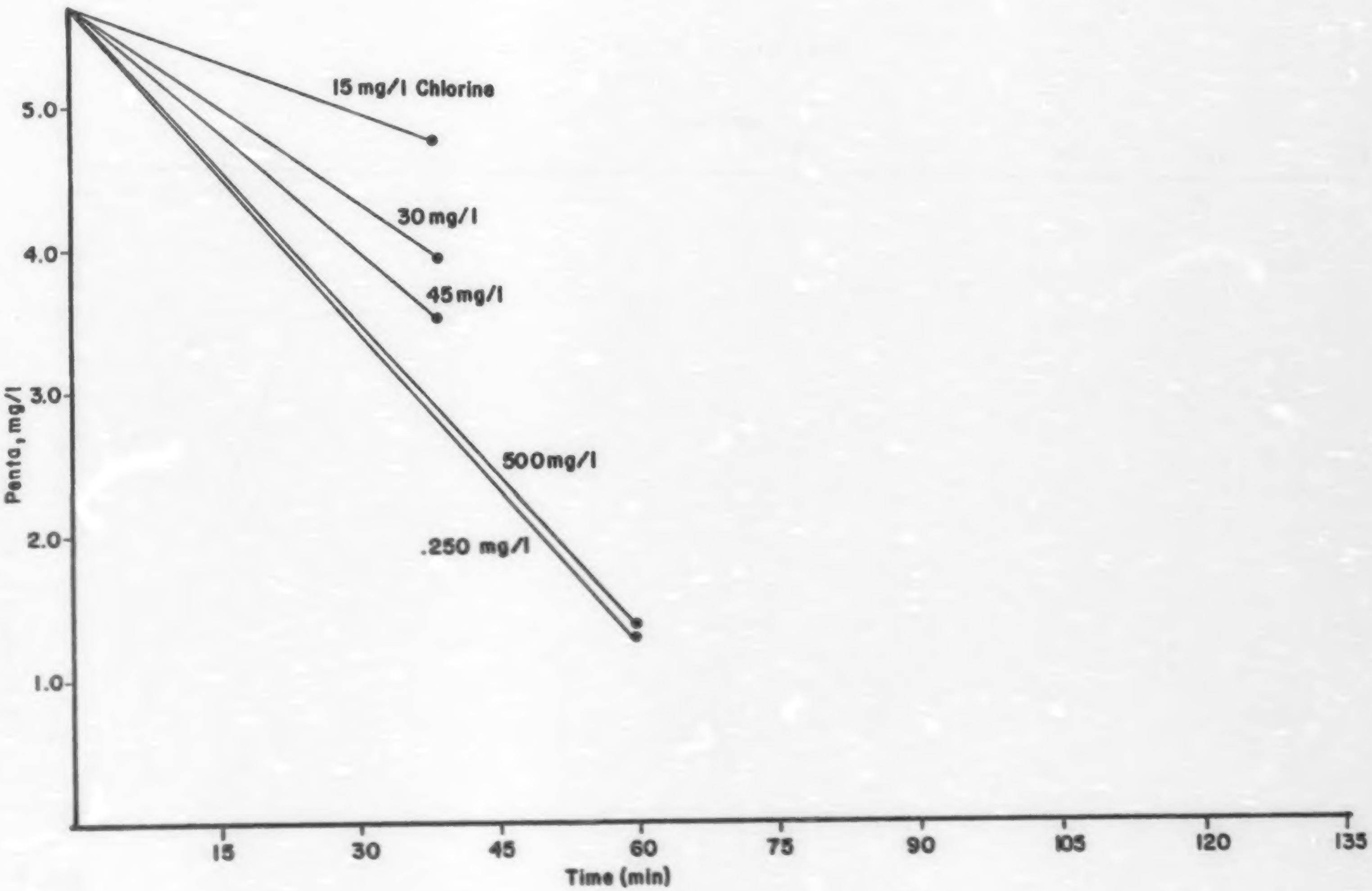

FIGURE 17.
Effects of Chlorine on Pentachlorophenol Concentrations as Measured by Safranin Method

TABLE 21.

EFFECTS OF FULL SCALE POST CHLORINATION

Date	Chlorine Feed (lb/day)	Chlorine Residual (mg/l)	Phenol, mg/l (1)	Phenol, mg/l (2)	Penta, mg/l (1)	Penta, mg/l (2)	COD, mg/l (1)	COD, mg/l (2)	BOD, mg/l (1)	BOD, mg/l (2)
2/11/74	0.75	2.0	0.6	0.6	8.4	4.4	595	595	125	95
2/14/74	0.75	0.5	0.5	0.5	7.6	5.3	645	670	80	75
2/18/74	1.0	3.3	0.4	0.4	8.1	5.2	755	760	95	80
2/21/74	3.0	11.1	0.9	0.9	9.2	4.3	700	735	110	85
2/25/74	5.0	24.4	1.2	0.6	9.6	3.2	855	835	265	95
2/28/74	7.0	32.0	0.8	0.4	8.2	1.4	835	860	100	80
3/4/74	10	35.7	1.1	0.6	9.4	5.2	805	800	125	65

(1) Before Chlorination
(2) After Chlorination

It should be noted that the nutrient levels during this period, as throughout the entire study, were quite elevated due to the previous use of a fire retardant which contained ammonia and phosphorus compounds. The presence of large concentrations of ammonium ions in the wastestream may have caused the high residuals of chlorine and contributed to the poor reaction of chlorine with the organics in the treated effluent.

PHASE 5- PRE-CHLORINATION

As has been previously discussed, the primary purpose of prechlorination was to reduce penta concentrations to a level that would allow satisfactory biological activity in the activated sludge process. It had been demonstrated during the previous phases of the project that pre-chlorination was not required in order to treat the wastes biologically. The need for pre-chlorination was therefore considered limited. However, before abandoning the concept entirely, it was decided to experiment on a laboratory scale with chlorination of the raw waste to determine if any measurable benefical effects occurred.

Initially, laboratory tests were conducted to determine chlorine persistence. This was considered important due to the high dosages which were expected to be required and because only small chlorine residuals could be allowed to enter the aeration units without damage to the activated sludge. Chlorine doses of approximately 600, 1200, 3400, and 6900 mg/l were prepared in the laboratory using sodium hypochlorite. Chlorine residual was measured with time over a period of at least 10 hours for each sample. The resulting chlorine residual curves are shown in Figure 18. It can be seen that the primary reaction of chlorine with the raw wastewater occurred within two to four hours and that the decrease in total residual occurred at a much slower rate after this initial period. After 19 hours of reaction time the sample initially treated with 600 mg/l of chlorine still contained a residual of over 200 mg/l. High initial doses resulted in correspondingly higher total residuals. The 6900 mg/l initial doses, for instance, produced a residual after 10 hours of over 2600 mg/l. Obviously, if large chlorine doses were required, high chlorine residuals would result and a substantial degree of dechlorination would be required before biological treatment would be possible.

Subsequent laboratory studies were conducted to determine the effects of chlorine on the raw waste at concentrations of chlorine of 500 mg/l and 1000 mg/l. As illustrated in Figure 19, oxidation of phenols occurred rapidly and completely at chlorine levels of 500 mg/l and 1000 mg/l. The reaction at pH 8 was somewhat more complete after one hour than the reaction at pH 2. Figure 20 shows penta removal with chlorine doses of 500 mg/l and 1000 mg/l. The efficiency of removal of penta was 40 percent using 500 mg/l of chlorine at pH 8, 81 percent using 500 mg/l of chlorine at pH 2 and about 80 percent using 1000 mg/l of chlorine at pH 8.

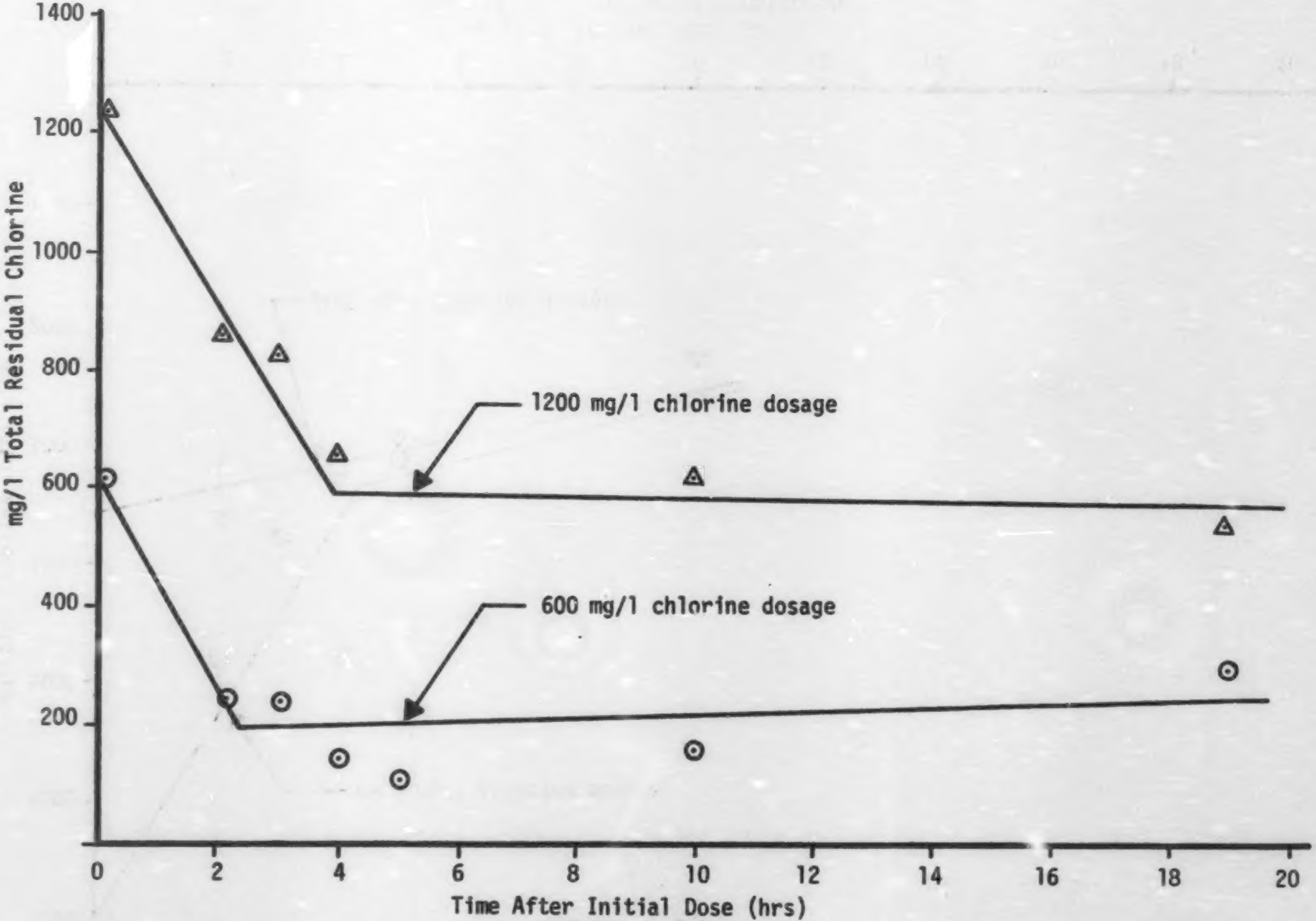

FIGURE 18 (a).
Chlorine Persistence

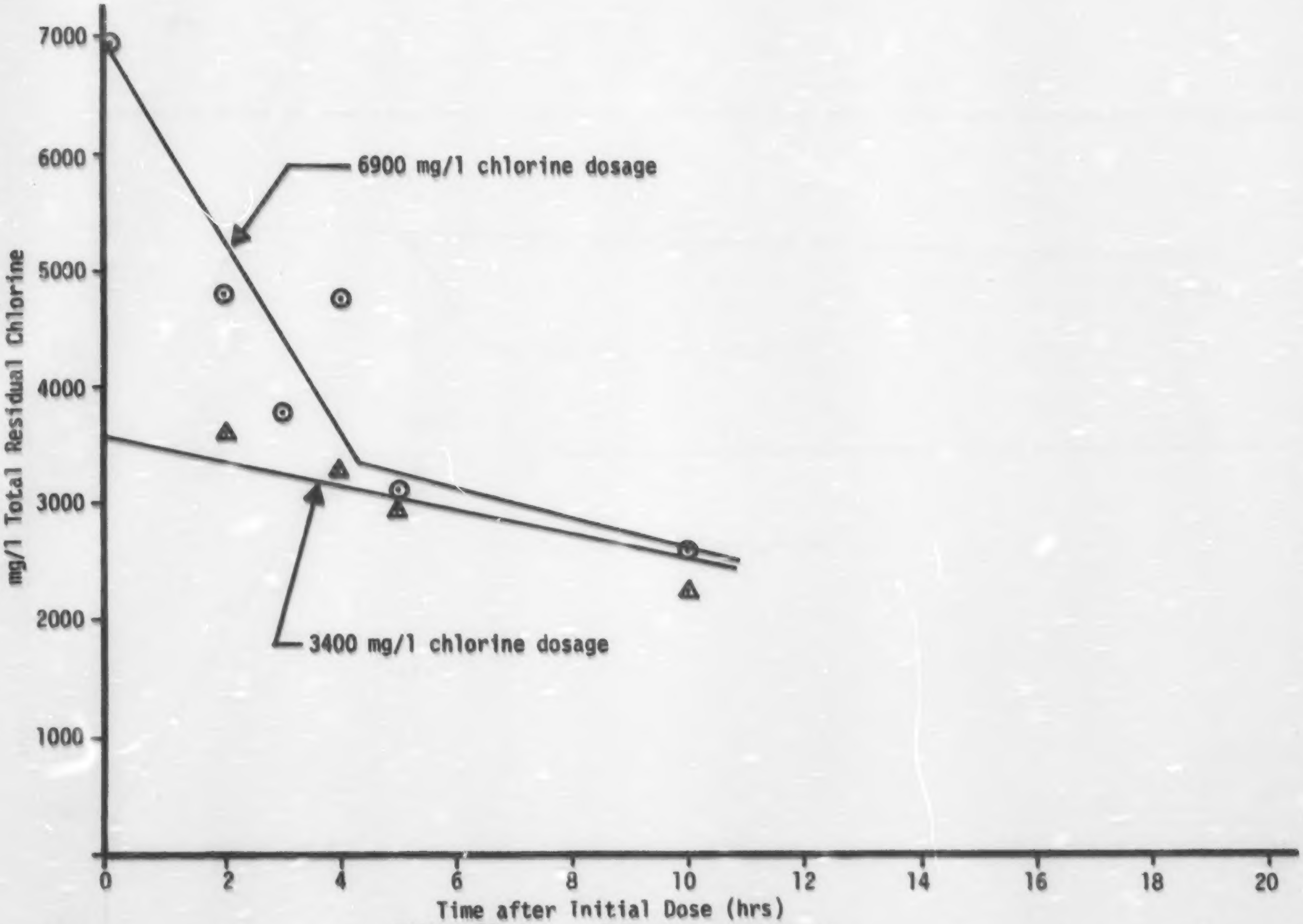

FIGURE 18 (b). Chlorine Persistence

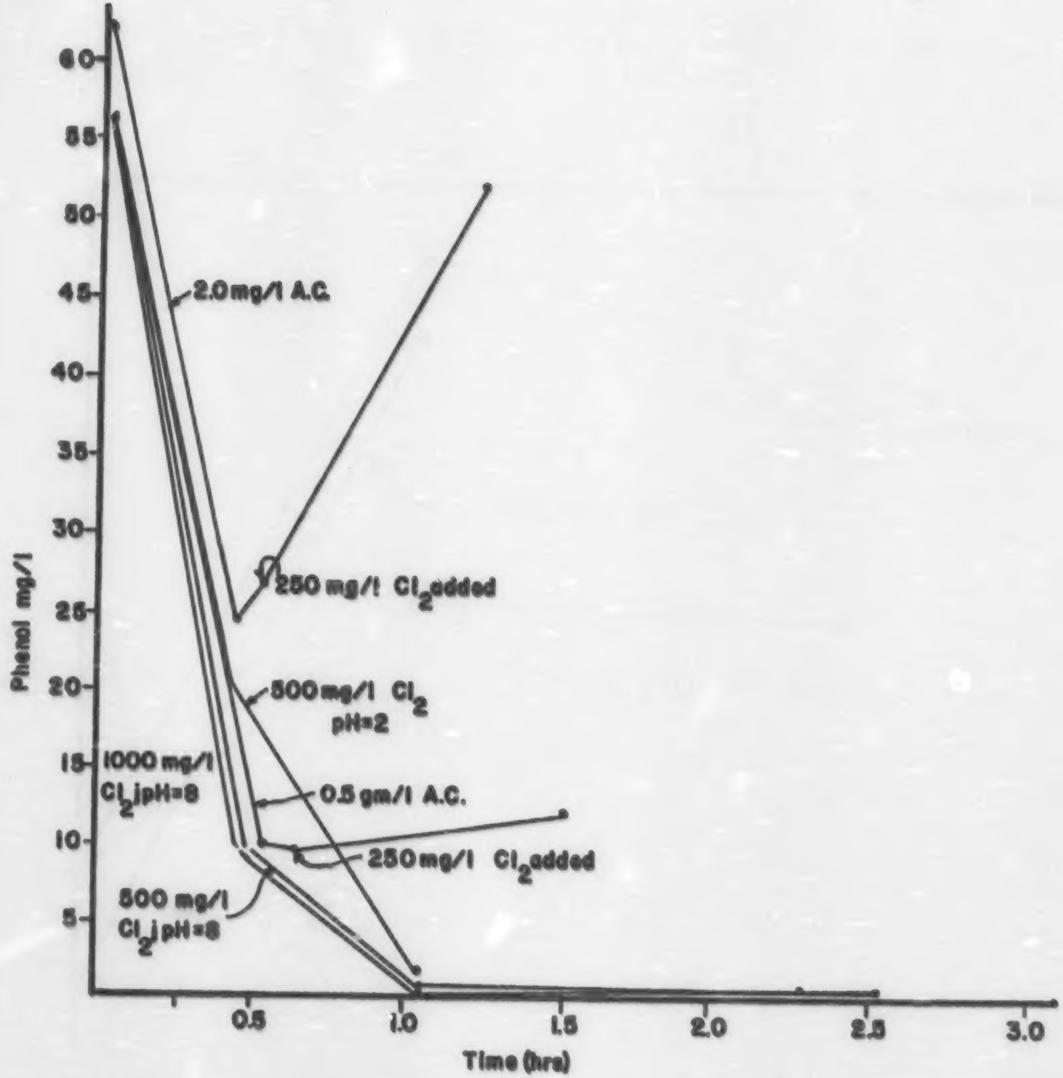

Figure 19. Effect of Chlorination on Phenolic Concentration of Raw Wastewater with Activated Carbon

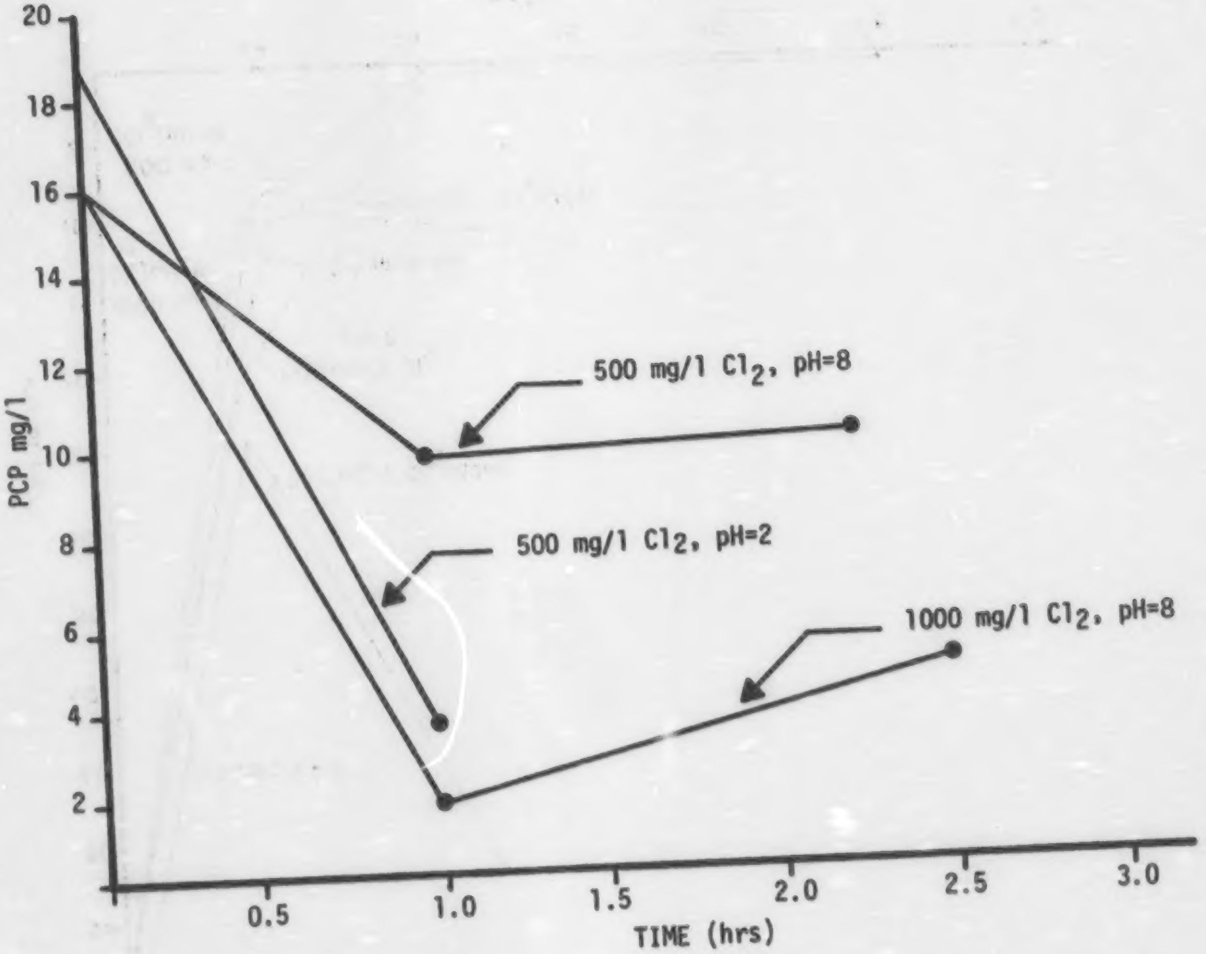

FIGURE 20.
Effect of Chlorination on Penta Concentration of Raw Wastewater with Activated Carbon

Also shown in Figures 19 and 20 is the effect of adding powdered activated carbon to the raw wastewater. As this was not part of the project objectives, the use of activated carbon was not studied extensively. However, the few tests performed indicated that activated carbon at a concentration of 0.5 grams/liter can reduce phenol concentration in the raw waste by 84 percent and penta by about 25 percent. At a concentration of 2.0 grams/liter, powdered activated carbon removed about 61 percent of the phenols and 98 percent of the penta.

It was thought that the adsorbed phenol and penta might be more readily oxidized either chemically or biologically while attached to the carbon than when in solution. Therefore, Figures 19 and 20 also show the results of a few experiments in which chlorine was added to a solution of powdered activated carbon and raw wastewater. The effect of the chlorine was apparently to attack the carbon preferentially resulting in the desorption of the phenol and penta molecules.

Based on the above results, it was intended that a full-scale pre-chlorination study be performed. A schedule of chlorine doses and dechlorinating agent requirements was prepared and pre-chlorination was begun on May 7, 1974. Due to the high chlorine residuals expected it was decided to initiate pre-chlorination at 50 mg/l and gradually increase the dosage to a maximum of 500 mg/l. Dechlorination was to be accomplished by the addition of sodium sulfite.

Pre-chlorination was continued for one month. Unfortunately, due to several problems, the chlorine dosage never exceeded about 75 mg/l and no significant reductions in phenol, penta, or COD were obtained. Problems related to pre-chlorination were largely operational. Dechlorination has not been anticipated to be a major problem in the initial design and, consequently, no alternatives other than air stripping were included in the treatment plant. Therefore, control of chlorine residual was accomplished during the study by gravity fed sodium sulfite, and the reliability of this system was poor. Consequently, either due to the chlorine or to excess sodium sulfite entering the aeration basin, the activated sludge process appeared to be suffering rather than benefitting from pre-chlorination. As can be seen by examination of the data contained in the Appendix, on May 28, 1974, phenol reduction efficiency appeared to be decreasing rapidly. Therefore, pre-chlorination was suspended on May 29.

DISCUSSION OF RESULTS

Based on the data developed during the study, the optimum design and operating parameters for the treatment of the specific wood preserving wastewater studied can be presented. As the characteristics of the waste are dependent upon the wood preserving process from which it comes, the design parameters for this waste may differ significantly from those at any other plant. However, the results and conclusions should allow generalizations for similar wood preserving plants.

It was determined early in the study that the wastewater inhibited the BOD test. While this fact precludes the use of the BOD test as a precise method of analysis, it does not eliminate its usefulness as an indicator. The average BOD/COD ratio of 0.35 was found to be rather constant for the raw waste.

The result of loading the activated sludge at various rates is summarized for COD in Figure 21. The percent reductions of COD when plotted against the nominal hydraulic detention time produce a linear relation as indicated. Increasing organic loading resulted in a linear decrease in treatment efficiency up to a loading of about 0.35 kg COD/day/dg MLSS, while the decrease in removal efficiency became much less rapid above the loading.

BOD and phenol concentration were readily reduced at practically every loading level tested. A BOD reduction of 90 percent and a phenol reduction of 99 percent were obtained.

The primary measurable effects of post-chlorination were to markedly improve the color of the wastewater and to reduce the penta concentration of the wastewater and/or the concentration of substances being measured as penta. Slight reduction of phenol and no reductions of organics were indicated under these operating conditions. At the conclusion of the EPA sponsored program, Koppers Company conducted a further investigation of post-chlorination. Preliminary results indicated that at a pH of 7 to 8 and a flow of 5.5 gpm, penta was reduced from about 5 mg/l to less than 0.10 mg/l.

Pre-chlorination was found to be effective for reducing penta and phenols in the raw waste. The ratio of chlorine to penta required to produce an 80 percent reduction in penta concentration was found to be in excess of 300:1 on a molar basis. In addition, the residual chlorine was found to be high following pre-chlorination, a condition which was possibly aggravated by the presence of ammonia. The high residual chlorine caused operational problems which were not overcome. Consequently, whether pre-chlorination could be beneficial to the activated sludge process was not clearly established.

Based on the results of this study, the following are design parameters for this particular waste:

Average COD loading = 0.3 kg/day/kg MLSS
Maximum COD loading = 0.4 to 0.5 kg/day/kg MLSS
Average BOD loading = 0.1 kg/day/kg MLSS
Maximum BOD loading = 0.2 kg/day/kg MLSS
Average phenol loading = 0.01 kg/day/kg MLSS
Average penta loading = 1.62 gm/day/cu m (0.1 lb/day/1000 cu ft)
Maximum penta loading = 6.5 gm/day/cu m (0.4 lb/day/1000 cu ft)
Average hydraulic detention time = 60 hours
Minimum hydraulic detention time = 40 hours

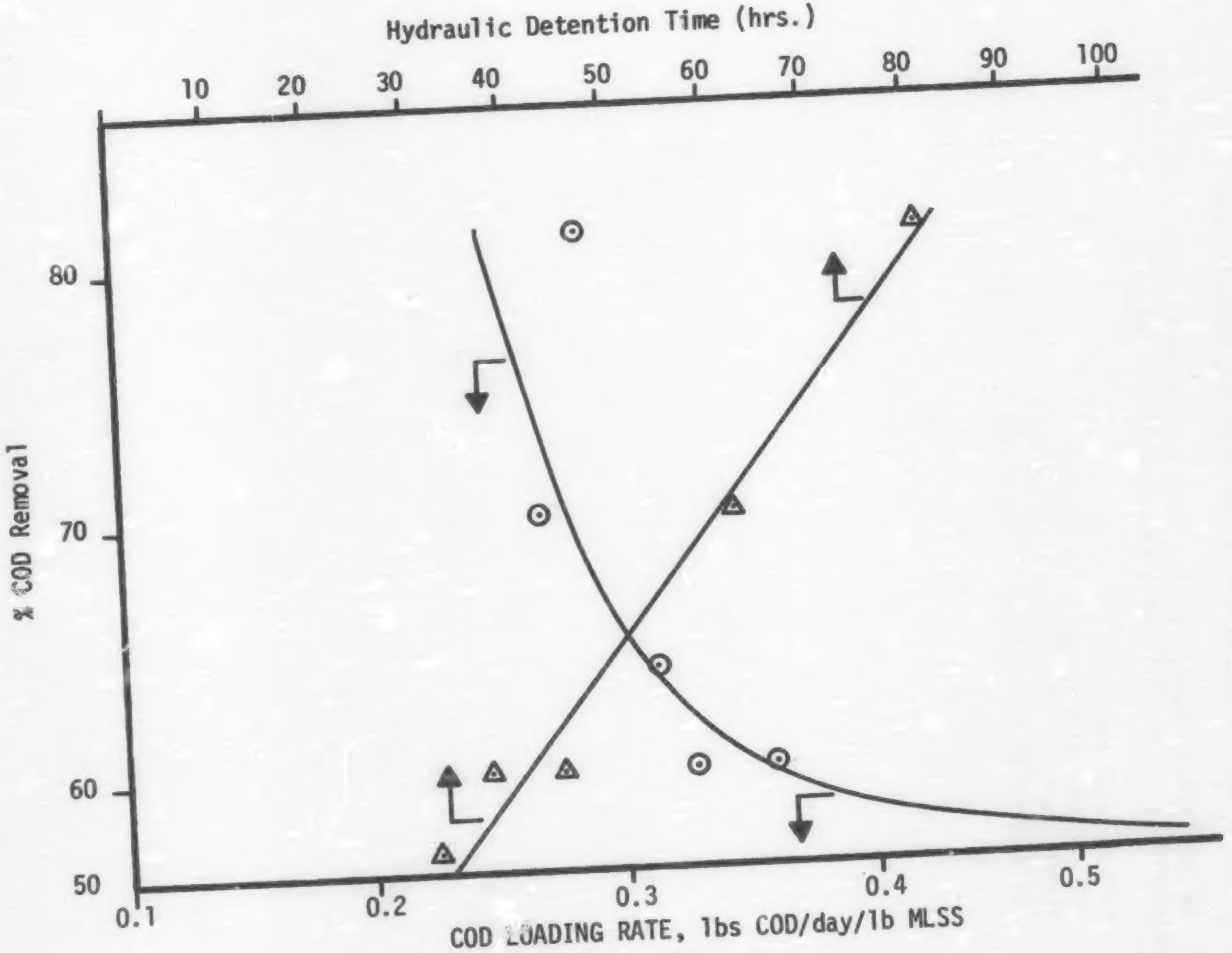

FIGURE 21.
COD Removal In The Activated Sludge Process

At the Carbondale wood preserving facility, the pretreatment system was adequate for recovering pentachlorophenol from the process waste stream prior to biological treatment. A properly designed and operated preservation recovery system in conjunction with equalization is important for successful operation at the loadings listed above.

An activated sludge process designed on the basis of the above should result in the following reduction efficiencies:

COD removal efficiency = 70 to 80 percent
BOD removal efficiency = 90 percent
Phenol removal efficiency = 99 percent
Penta removal efficiency = 99 percent

SECTION VII

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SECTION VIII

GLOSSARY

Activated Sludge - Sludge floc produced in raw or settled wastewater by the growth of zoogleal bacteria and other organisms in the presence of dissolved oxygen and accumulated in sufficient concentration by returning floc previously formed.

Aerated Lagoon - A natural or artificial wastewater treatment pond in which mechanical or diffused-air aeration is used to supplement the oxygen supply.

Alum - A common name in the water and wastewater treatment field for commercial-grade aluminum sulfate.

Bentonite - An absorptive and colloidal clay used especially as a filler (as in paper) or carrier (as of drugs).

BOD - Biological Oxygen Demand is a measure of biological decomposition of organic matter in a water sample. It is determined by measuring the oxygen required by microorganisms to oxidize the organic contaminants of a water sample under standard laboratory conditions. The standard conditions include incubation for five days at 20°C.

COD - Chemical Oxygen Demand. Its determination provides a measure of the oxygen demand equivalent to that portion of matter in a sample which is susceptible to oxidation by a strong chemical oxidant.

Creosote - A complex mixture of organic materials obtained as a by-product from coking and petroleum refining operations that is used as a wood preservative.

Cresol - Any of three poisonous colorless crystalline or liquid isomeric phenols C_7H_8O.

Emulsion - A heterogeneous liquid mixture of two or more liquids not normally dissolved in one another, but held in suspension one in the other by forceful agitation or by emulsifiers which modify the surface tension of the droplets to prevent coalescence.

Flocculation - In water and wastewater treatment, the agglomeration of colloidal and finely divided suspended matter after coagulation by gentle stirring by either mechanical or hydraulic means. In biological wastewater treatment where coagulation is not used, agglomeration may be accomplished biologically.

Lime - Any of a family of chemicals consisting essentially of calcium hydroxide made from limestone (calcite) which is composed almost wholly of calcium carbonate or a mixture of calcium and magnesium carbonate.

Mixed Liquor - A mixture of activated sludge and organic matter undergoing activated sludge treatment in the aeration tank.

Pentachlorophenol - A crystalline compound C_6Cl_5OH used as a wood preservative, fungicide and disinfectant.

Phenol - The simplest aromatic alcohol.

Polyelectrolyte - A nonmetallic electric conductor of high molecular weight in which current is carried by the movement of ions.

Quinone - Either of two isomeric cyclic crystalline compounds $C_6H_4O_2$ that are di-keto derivatives of dihydro-benzene.

Sludge Volume Index (SVI) - It is the volume in milliliters occupied by 1 gm of activated sludge after settling of the aerated liquid for thirty minutes.

Thiocyanate - A salt or ester of thiocyanic acid, a colorless unstable liquid acid (HSCN) of strong odor.

Trickling Filter - A filter consisting of an artificial bed of coarse material, such as broken stone, clinkers, slate, slats, brush, or plastic materials, over which wastewater is distributed or applied in drops, films, or spray from troughs, drippers, moving distributors, of fixed nozzles, and through which it trickles to the underdrains, giving opportunity for the formation of zoogleal slimes which clarify and oxidize the wastewater.

SECTION IX

APPENDIX

OPERATIONS LOG

The treatment facilities at Carbondale were placed in operation on July 26, 1973 and the testing program was terminated on May 31, 1974. Table A presents a summary of key data collected during the study. Following is a condensation of the daily log maintained by the treatment plant operators:

August 1973

The activated sludge plant was installed and filled with water from the emergency lagoon. Horse manure was used as a seed and aeration began on July 26. The reason for using water from the emergency lagoon initially was that it had relatively low concentrations of phenol, penta, and boron and its pH was near neutrality. Subsequently, wastewater from Lagoon No. 1 was gradually added. Three thousand gallons of water from Lagoon No. 1 were added on July 31. Until August 20 the influent to the activated sludge system consisted of a mixture of waters from the emergency lagoon and Lagoon No. 1, but on that date the emergency lagoon pump broke down and problems developed with the pump on Lagoon No. 1. Although both pumps were repaired on August 23, it was decided to continue use of only water from Lagoon No. 1, and to increase the flow by one gallon per minute each day until a flow of 6 gpm was obtained.

It was observed that almost no suspended solids were building up in the aeration tanks. On August 13 floating sludge was observed in the clarifier. Although sludge was returned to aeration at maximum capacity, the problem continued. On August 28 it was discovered that a pin had sheared in the clarifier paddle assembly preventing aeration of the paddles. The clarifier was emptied into the aeration tank and repairs were made.

Considerable amounts of protozoa were observed from initial start-up until August 21 when the numbers began to drop drastically. Small amounts of lime were added to Aeration Tank No. 1 to increase the pH, and the protozoa count increased.

Due to lack of power at the on-site laboratory, penta analyses were not begun until August 21.

September 1973

The month of September was intended as a sludge build-up period. Settleable solids increased from 35 ml/l at the beginning of September to 180 ml/l at the end of the month. By the end of the month the MLSS was about 2000 mg/l.

The water level in Lagoon No. 1 was getting low enough that the pump began to pick up debris from the bottom, so water was added to Lagoon No. 1 from Lagoon No. 3. This temporarily lowered the concentration of penta and phenol entering the activated sludge system, but as raw wastes continued to be added to Lagoon No. 1, these concentrations began to rise.

October 1973

On October 8, by which time the MLSS of both aeration tanks averaged about 2500 mg/l and settleable solids about 270 ml/l, the feed rate was set at 11 gpm and maintained at that rate through October 10. From October 11 through October 14 the feed was reduced to 5.5 gpm while the aeration tanks were being sprayed with an insulation material and painted.

As indicated in Table A, the flow rate of 11 gpm resulted in a reduced efficiency as phenol removal. So on October 15, when both aeration tanks were back in operation it was decided to raise the feed rate gradually while allowing the system to adjust and reduce phenol levels prior to each increase. It took four days to again achieve a flow of 11 gpm. The rate of 11 gpm was maintained from October 18 through October 25 with only a slight loss in phenol removal efficiency. On October 26 the flow was reduced to 5.5 gpm to allow stabilization in preparation for tripling the feed rate.

As can be seen in Table A, the pH of the influent to the activated sludge system was consistently below 5.0. Prior to the feed increase on October 8, only periodic additions of small amounts of lime were necessary to maintain a pH in the aeration tank at above 6.0. However, after the flow was increased on October 8, considerably larger lime dosages were necessary nearly every day.

November 1973

On November 7 the feed rate was increased from 5.5 to 7 gpm and then gradually increased to 13 gpm by November 12. This rate was maintained for three days, at which time drastically reduced phenol removal necessitated a feed reduction. Six gallons per minute were fed until the holiday weekend of November 22 during which time the flow was cut off and the air supply decreased.

The reason for shutting off the flow was that many wood preserving plants do not have the lagoon capacity that the Carbondale facility does and no flow on a long weekend would be normal. Also, in an effort to conserve electricity (the winter of 1973 found the United States in an "Energy Crisis"), the metabolism of the sludge was reduced by timing the air pumps to run for one hour and be off for five hours.

Large quantities of lime were necessary to maintain the pH in the aeration basins near neutrality. This was especially true during the period of high feed rate.

Protozoa were easily visible until the system upset of November. 15. On November 16 horse manure was added to replace protozoa.

December 1973

The stabilization period of the last week in November was maintained into December. On December 3 heaters were installed in the aeration tanks and these were expected to maintain a water temperature of at least 20°C.

On December 3 the water temperature was 15°C. By the next day the heaters had increased it to 17°C; however, the temperature then dropped until by December 7 it was at 11°C.

During the weekend of December 8 and 9 the flow was cut off and the air pumps were operated for one hour of each six hours. This did not allow adequate water circulation over the immersion heaters; they developed a sludge layer and burned out. The lack of circulation also led to freezing of several lines and both pumps in Lagoon No. 1. There was a thin layer of ice on all tanks.

By December 13 the system had thawed enough that repairs could be begun.

More cold weather appeared on December 19 and from that date until December 25 there was at least a four inch layer of ice on all tanks. All operations were suspended.

The plant was back in operation on December 26. Then, on December 29, a line became clogged with ice and the system became frozen again.

January 1974

It was decided that for the remainder of the study only Aeration Tank No. 1 would be used in order to allow better operational control. On January 8 new heaters were installed in the aeration tank by chopping through five inches of ice. By January 10 the aeration tank had thawed, but the external valves and lines were still frozen. On January 17 the system was placed in operation with a flow of 1.5 gpm. Also on January 17, heaters were installed in the pre-chlorination unit. The temperature in the aeration basin gradually increased but did not rise above 20°C until January 21.

The flow was gradually increased until it reached 4 gpm on January 28 (it would be maintained at this rate until March 11).

On January 23 a program of wasting small amounts of sludge to the digester was initiated. The MLSS at this time was 4650 mg/l, and it was intended to eventually reduce it to 3500 mg/l.

February 1974

By the beginning of February the activated sludge system was operated as designed and as soon as the MLSS became stationary it was planned to begin post-chlorination.

By February 7 the MLSS was below 3800 mg/l and post-chlorination was initiated at 7 pounds of chlorine per day. This resulted in a chlorine residual of 35 mg/l.

It was decided to determine what chlorine feed rate would yield a residual of near 1 mg/l. February 10 through 14 results on Table B show a feed of 0.75 ppd would achieve a residual of about 1 mg/l.

It was also intended to increase the chlorine feed gradually to a maximum of 10 ppd to determine effects of BOD, COD, penta, and phenols. This was done from February 15 through March 4. From February 22 through March 4 the pH of the post-chlorinated water began to drop drastically as the chlorine feed approached 10 ppd.

March and April 1974

The objective during March and April was to determine the effects of increased flow rates while maintaining other factors constant. Throughout the two-month period it was necessary to add large amounts of lime (12 to 16 pounds every second or third day) in order to control pH in the aeration basin.

On March 7 the line between the aeration basin and the clarifier became clogged. This caused the aeration basin to overflow and lose solids.

Beginning March 9 flow rates were increased until March 17. On March 16 the sludge return line became clogged and large amounts of sludge had to be wasted in order to unclog the line. Horse manure was added to the aeration basin on March 13 to increase the protozoa count.

Beginning on March 19 the flow rate was again increased until it reached 6.5 gpm on March 22. At this point the phenol concentration in the effluent had risen to such a high level that the flow was reduced to 3 gpm to allow system stabilization.

Sludge had to be wasted almost daily in order to maintain a MLSS of approximately 3500 mg/l. On March 21 phenols and penta concentrations were observed to be low in the digester. It was decided to incorporate a sludge contact chamber. On March 26 all return sludge was pumped to the digester for two hours detention before being returned to the aeration basin. Using the contact tank, the flow was gradually increased until April 8 when the submersible pumps went out. The system was immediately converted back to straight activated sludge.

The feed rate was continually increased, despite increased phenol concentrations in the effluent, until April 29 when sludge began to float in the clarifier.

On April 11 the penta oil separation system malfunctioned and penta was spilled into Lagoon No. 1. On April 15 the spill began to appear in the treatment system.

May 1974

The primary objective during May was to determine the effects and operating parameters of pre-chlorination. The flow rate was set at 6 gpm. It was intended to maintain a MLSS of 3500 mg/l, but, as shown in Table A, the MLSS varied from 2790 to 4320 mg/l.

Pre-chlorination began at 50 mg/l and was scheduled to be increased to 500 mg/l during the month. Sodium sulfite was used for de-chlorination prior to aeration. Sodium hydroxide was used to maintain a pH of 7 to 8 in the aeration basin.

Pre-chlorination was initiated on May 7 at 50 mg/l. No residual resulted. On May 9 the chlorine feed rate was increased to 75 mg/l and a residual of 1 to 2 mg/l resulted.

Due to the fact that extreme difficulties were encountered in controlling the sodium sulfite addition by the gravity feed system, it was decided to install a feed pump. The pre-chlorination feed rate was maintained at 75 mg/l until the pump could be installed.

The feed pump was received on May 22 and prepared for installation. However, on May 28 it became apparent from increasing phenol levels in the effluent that the activated sludge system was breaking down. The pre-chlorination schedule was discontinued.

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH		Phenol (mg/l)		Penta (mg/l)		BOD (mg/l)		COD (mg/l)		PO_4 (mg/l)		NH_4 (mg/l)		SS (mg/l)		DO in Aeration (mg/l)		MLSS (mg/l)	
			Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	#1	#2	#1	#2
7/26/73	Aeration Basin																					
7/31/73	Wastewater Added																					
8/2/73																						
8/31/73		5																				
8/4/73		5	5.9	6.1	0.4	0.6																
8/5/73		5			12	<1																
8/6/73		5	5.8	6.4	15	<1																
8/7/73		5	5.8	6.3	27	<1																
8/8/73		5	5.8	6.4	30	<1																
8/9/73		5	5.5	6.4	65	1																
8/10/73		5	5.4	6.5	65	1.4									-	40						
8/13/73	Rising Sludge	5	5.5	6.5	65	1.6																
8/14/73		5	5.5	6.5	75	1.5																
8/15/73		5	5.4	6.5	65	1.5																
8/16/73		5	5.5	6.5	70	2.0																
8/17/73		4.5	5.5	6.5	70	2.0																
8/21/73	Pump Problems	2	5.4	6.2	70	1.5	3.4	0.6			1260	350										
8/22/73		2	5.5	6.1	70	1.5	3.4	0.3														
8/23/73	Pumps Corrected	3	5.5	6.2	70	2.0	2.3	0.86					-	440	-	67						
8/24/73	Lime Added	4	5.4	6.2	70	1.0	2.6	0.3														
8/25/73		5	-	6.2	-	2.0																
8/26/73		5	-	6.2	-	3.0																
8/27/73		6	5.2	6.5	80	2.0																
8/28/73	Clarifier Paddles Corrected	6	5.3	6.3																		
8/30/73		6	5.0	6.6	85	2.0					1820	470										
8/31/73		6	5.1	6.6	95	2.0																
9/4/73		6	5.0	6.5	90	1																
9/5/73		6	4.9	6.7	90	2	2.2	0.6			1960	440										
9/6/73		6	3.9	6.6	95	1	2.7	0.5					-	380	-	67						
9/7/73	Lime Added	6	5.0	6.4	95	2																

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH Inf.	pH Eff.	Phenol (mg/1) Inf.	Phenol (mg/1) Eff.	Penta (mg/1) Inf.	Penta (mg/1) Eff.	BOD (mg/1) Inf.	BOD (mg/1) Eff.	COD (mg/1) Inf.	COD (mg/1) Eff.	PO_4 (mg/1) Inf.	PO_4 (mg/1) Eff.	NH_4 (mg/1) Inf.	NH_4 (mg/1) Eff.	SS (mg/1) Inf.	SS (mg/1) Eff.	DO in Aeration (mg/1) #1	DO in Aeration (mg/1) #2	MLSS (mg/1) #1	MLSS (mg/1) #2
9/10/73		6	5.2	6.6	70	<1	1.7	0.6														
9/12/73		6	5.5	6.5	70	<1					1550	400										
9/13/73		6	5.1	6.5	70	1	1.8	0.3					-	430	-	57						
9/14/73		6	5.0	6.5	95	1																
9/17/73		6	5.0	6.5	90	<1	1.6	0.1														
9/18/73		6	5.0	6.6	90	1					1700	400	-	400	-	67						
9/19/73		6	5.0	6.4	90	1	1.5	0.3														
9/20/73		6	4.9	6.4	90	1																
9/21/73		6	4.9	6.3	90	1	1.5	0.2														
9/24/73		6	4.9	6.2	90	1	1.2	0.3														
9/25/73		6	4.9	6.4	90	<1					1925	375										
9/27/73		6	4.9	6.2	100	1																
9/28/73		6	4.8	6.1	100	1	1.7	0.5					-	360	-	55						
10/1/73		6	4.7	6.0	100	2	1.53	0.64									-	106			2426	1751
10/2/73		6	4.7	6.2	110	2					2272	612										
10/3/73		6	4.7	6.2	100	1	1.73	0.64					-	350	-	50						
10/4/73		6	4.7	6.2	100	1																
10/5/73		6	4.5	6.2	100	1	1.82	0.97														
10/8/73	Added Lime	11	4.7	6.0	110	1	1.35	0.57														
10/9/73	Added Lime	11	4.7	6.1	110	3					2647	708									4050	3690
10/10/73		11	4.6	6.3	120	9	1.62	1.32	415	40												
10/11/73	Tank Maintenance	5.5	4.7	6.2	90	10																
10/12/73		5.5	4.7	6.3	100	7	2.36	1.62														
10/15/73	Added Lime	7	4.8	6.2	75	1	2.15	1.62														
10/16/73		9	4.8	6.4	75	1																
10/17/73	Added Lime	9	4.8	6.2	80	1					2117	757										
10/18/73		11	4.8	6.1	90	2	2.15	2.15														
10/19/73	Added Lime (10/19-10/22)	11	4.7	6.2	75	1	2.28	1.78	755	75			-	340							3650	2640

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH		Phenol (mg/1)		Penta (mg/1)		BOD (mg/1)		COD (mg/1)		PO_4 (mg/1)		NH_4 (mg/1)		SS (mg/1)		DO in Aeration (mg/1)		MLSS (mg/1)	
			Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	#1	#2	#1	#2
10/23/73		11	4.8	6.4	75	3	1.68	2.02														
10/24/73		11	4.8	6.3	70	3					2117	846										
10/25/73		11	4.8	6.4	70	2							-	460	-	45						
10/26/73	Added Lime	5.5	4.9	6.4	70	3	2.22	2.56	860	63												
10/29/73		5.5	4.8	6.4	90	2	1.93	2.15														
10/30/73	Added Lime	5.5	4.8	6.4	80	1	2.30	3.13														
10/31/73		5.5	4.8	6.7	90	1					2217	803										
11/1/73		5.5	4.8	6.7	80	1							-	320	-	55					4280	3500
11/2/73	Added Lime	5.5	4.8	6.7	90	1	2.3	2.4	1045	110									2.5	7.8		
11/5/73		5.5	4.8	6.6	90	1	2.1	2.3														
11/6/73		5.5	4.8	6.6	90	1					2290	730										
11/7/73		7	4.8	6.6	90	2	2.1	2.1											3.0	9.5		
11/8/73	Began Regular Lime Addition	9.5	4.9	6.6	100	1							-	300	-	52					4940	3800
11/9/73		11	4.7	6.6	90	2	2.4	2.2											2.5	4.5		
11/12/73		13	4.7	6.6	80	2	2.7	3.3														
11/13/73	Poor Sludge Separation	13	4.8	6.8	90	10					2650	1040										
11/14/73		13	4.7	6.7	90	20	3.1	2.7											1.3	1.5		
11/18/73	No Feed (11/15,11/16)	6	-	6.9	-	4															5250	4930
11/19/73		6	4.7	6.9	90	4	4.4	3.8														
11/20/73		6	4.7	6.7	90	2					2910	1090									5340	4970
11/21/73		6	4.7	6.8	90	1	4.4	3.5					-	260	-	40			1.0	3.5		
11/26/73	No Feed (11/22-11/25)	6	4.8	6.8	70	2																
11/27/73		6	4.8	6.9									-	260	-	45	120	270	1.5	1.5		
11/28/73		6	4.8	6.8															2.0	6.0	5110	4660
11/29/73		6					4.6	4.3			2240	1030							2.3	7.5		

TABLE A

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH		Phenol (mg/1)		Penta (mg/1)		BOD (mg/1)		COD (mg/1)		PO_4 (mg/1)		NH_4 (mg/1)		SS (mg/1)		DO in Aeration (mg/1)		MLSS (mg/1)	
			Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	#1	#2	#1	#2
11/30/73		6	4.8	6.9					780	100							110	200	2.2	9.0	5180	4090
12/3/73	Heaters Installed	6	4.7	6.9	54	0.7	4.1	4.1			2100	1000							2.0	8.5		
12/4/73		6	4.7	7.0									220	200	60	40	90	200	1.5	6.5	5000	3940
12/5/73		6	4.9	7.1	55	0.5	4.5	4.9			2110	940							2.2	7.5		
12/6/73		6	4.8	6.9									200	200	60	42	100	160	2.9	5.5	5040	4420
12/7/73		6	4.8	6.9	56	0.4	4.1	4.0	985	103	2040	820							2.8	7.8		
12/10/73	Lagoon Pump Frozen	0																	3.2	5.0		
12/12/73		6	4.8	7.2	54	0.9	3.8	4.3			2150	960										
12/13/73		6	4.8	7.0									300	260	60	35	60	120	5.0	7.5	5190	4540
12/14/73	#1 Tank Repair Begun	3	4.7	6.9	55	0.7	4.9	5.9	1065	125	2180	880							-	5.8		
12/17/73		3	4.8	6.7	55	5.1	4.2	4.8			2170	910							-	7.5		
12/18/73		3	4.7	6.9									240	240	65	55	100	160	-	9.5	3570	4860
12/19/73		3	4.8	6.9	56	13	4.1	5.2	821	-	2110	1060										
12/26/73		3	4.8	7.0	35	1.5	3.7	4.5														
12/27/73		3	4.9	-																	4900	4080
12/28/73	Both Tanks in Operation	1.5	4.8	7.1	44	0.7	3.4	4.9			1620	990										
1/15/74	No Flow	0																			3810	4880
1/18/74	Flow Into #1 Only	1.5	4.8	6.9	42	0.4	4.0	4.6	540	85	1610	690							3.0	-		
1/21/74		2.5	4.8	7.4	38	0.1	4.2	5.0			1730	690							2.0	-		
1/22/74	Increased Air	3	4.9	7.1									200	200	55	55	80	110	0.5	-	4650	-
1/23/74		3	4.8	7.2	43	0.2	3.0	4.3			1730	590							2.2	-		
1/24/74		3	4.9	7.0									200	200	60	45	100	150	1.6	-	4620	-
1/25/74		3	4.8	7.1	43	0.1	3.6	4.2	695	100	1730	610							2.0	-		
1/28/74	Air Pump Break Down	4	4.8	6.7	44	0.4	3.0	3.8	790	135	1640	710							0.5		4610	
1/29/74		4	4.9	6.6									260	200	55	45	130	170	0.5	-		

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH		Phenol (mg/l)		Penta (mg/l)		BOD (mg/l)		COD (mg/l)		PO_4 (mg/l)		NH_4 (mg/l)		SS (mg/l)		DO in Aeration (mg/l)		MLSS (mg/l)	
			Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	#1	#2	#1	#2
1/30/74		4	4.8	6.5															1.0		4340	-
1/31/74		4	4.8	6.8	52	0.2	3.5	4.9	515	85	1830	570							1.0			
2/1/74		4	4.8	6.7													90	100	1.0	-	4125	-
2/4/74		4	4.8	6.8	56	0.4	4.0	5.7	1040	220	2110	605							1.0	-	3375	-
2/6/74		4																	2.5	-	3860	-
2/8/74		4	-	5.8					520	55									2.4	-	3620	-
2/11/74		4	4.9	6.4	62	0.6	5.1	4.4	465	95	2340	595							3.0		3880	-
2/12/74		4	4.8	6.8									220	180	55	30	115	100	2.1	-		
2/13/74		4	4.8	6.6															2.0	-	3780	-
2/14/74		4	4.8	6.6	59	0.5	3.9	5.3	565	75	2450	570							1.5	-		
2/15/74		4	4.8	6.5													110	90	1.5		3660	-
2/18/74		4	4.8	6.6	58	0.4	5.2	5.2	630	80	2390	760							0.5	-	3760	-
2/19/74		4	4.9	6.0									200	160	60	40	175	110	1.9	-		
2/20/74		4	4.8	5.7															2.5	-	3390	-
2/21/74		4	4.9	6.2	62	0.9	7.4	4.3	730	85	2420	735							0.4	-		
2/22/74		4	4.9	5.6													160	115	0.5	-	3610	-
2/25/74		4	4.9	4.2	64	0.6	6.0	3.2	1070	95	2500	835							3.5	-	3765	-
2/26/74		4	5.3	4.7									220	180	70	50	140	110	2.5	-		
2/27/74		4	5.0	3.7															1.5	-		
2/28/74		4	5.0	4.6	63	0.4	3.2	1.4	740	80	2630	[illegible]							2.2	-		
3/1/74		4	5.1	3.3													160	135	0.5	-	3585	-
3/4/74		4	5.0	3.0	70	0.6	5.4	5.2	920	65	2800	800							0.5	-	4155	-
3/5/74		4	5.1	6.9									200	200	65	40	850	700	1.7	-		
3/6/74		4	5.1	6.9															2.2	-	3930	-
3/7/74		4																	1.0	-	2750	-
3/8/74		4	5.0	6.9	66	0.2	7.8	7.4	860	85	2965	722							2.0	-	3445	-
3/11/74		5	4.7	6.5	60	0.6	8.6	8.6	770	95	2620	855							1.5	-	4290	-
3/12/74		5	4.9	6.7									180	180	60	25	175	165	1.7	-		
3/13/74	Added Horse Manure	5	4.7	6.8															1.2	-	4395	-
3/14/74		5	4.7	6.7			7.5	8.1	1015	135	2715	985							1.2	-	3775	-

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH Inf.	pH Eff.	Phenol (mg/1) Inf.	Phenol (mg/1) Eff.	Penta (mg/1) Inf.	Penta (mg/1) Eff.	BOD (mg/1) Inf.	BOD (mg/1) Eff.	COD (mg/1) Inf.	COD (mg/1) Eff.	PO_4 (mg/1) Inf.	PO_4 (mg/1) Eff.	NH_4 (mg/1) Inf.	NH_4 (mg/1) Eff.	SS (mg/1) Inf.	SS (mg/1) Eff.	DO in Aeration (mg/') #1	DO in Aeration (mg/') #2	MLSS (mg/1) #1	MLSS (mg/1) #2
3/15/74		5	4.7	6.9													180	65	1.0	-	3805	-
3/16/74	Sludge Return Line Clogged	5.5																				
3/17/74		5.5																	2.7	-	1645	-
3/18/74		4	4.7	6.9	65	0.5	7.2	9.1	830	100	2245	700							3.0	-	3530	
3/19/74		5	4.8	6.9													160	100	1.4	-		
3/20/74		5.5	4.7	6.9									160	160	50	35			3.0	-	3605	-
3/21/74		6	4.8	6.7	59	1.2	8.1	9.9	910	115	2455	725							3.5	-		
3/22/74		6.5	4.8	6.9	60	5.0	7.4	7.0									80	120	3.0	-	3350	-
3/25/74		4	4.8	6.8															4.0	-		
3/26/74	Started Returning Sludge	4																			3785	-
3/27/74	To Contact Tank For 2 hr	4	4.9	6.7															4.0	-	2920	-
3/28/74	Then to #1 Tank	4	4.8	6.8	63	0.3	6.6	6.2	875	95	2400	720							2.8	-		
3/29/74		4	4.8	6.8													145	145	2.2	-	3315	-
4/1/74		4	4.8	6.8	60	0.2	6.1	6.5	750	120	2365	710							3.5	-	3040	-
4/2/74		5	4.9	6.8													140	135	2.5	-		
4/3/74		5	4.8	6.8									160	140	60	40			2.5	-	3320	-
4/4/74		5	4.8	6.8	64	0.2	6.4	6.8	865	100	2375	-							3.0	-	2910	-
4/5/74		5.5	4.8	6.8													105	155	3.5	-	3355	-
4/8/74	Stop Use of Contact Tank	5.5	4.8	6.6	60	0.2	6.7	6.4	945	115	2285	650							4.0	-	3780	-
4/9/74		5.5	4.7	6.8									125	125	65	60	110	135	4.0	-	4220	-
4/10/74		6	4.7	6.7															2.7	-	3980	-
4/11/74		6	4.7	6.7	58	9.5	7.1	7.2	995	135	2580	790										
4/12/74		6	4.7	6.6													320	155	2.0	-	4385	-
4/15/74		6	4.7	6.8	59	0.3	8.6	10.4	845	120	2640	1070							3.0	-	4880	-

TABLE A.

DAILY LOG SUMMARY

DATE	REMARKS	Flow (gpm)	pH		Phenol (mg/1)		Penta (mg/1)		BOD (mg/1)		COD (mg/1)		PO$_4$ (mg/1)		NH$_4$ (mg/1)		SS (mg/1)		DO in Aeration (mg/1)		MLSS (mg/1)	
			Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	Inf.	Eff.	#1	#2	#1	#2
4/16/74		6.5															225	210	3.5	-	5070	-
4/17/74		6.5																	5.0	-	3710	-
4/22/74		7.5																	3.5	-		
4/23/74		7.5	4.9	6.6	56	2.3	15.8	17.2													4225	-
4/24/74		8	4.7	6.7									120	120	60	40			1.2	-	4050	-
4/25/74		8	4.7	6.9	65	0.5	11.2	22.4	885	100	2595	1155							1.3	-		
4/26/74		8	4.8	6.6													1[illegible]0	90	0.5	-	4260	-
4/29/74	Rising Sludge	8	4.7	6.8	64	0.4	7.6	15.2	935	95	2465	1100							3.0	-	3285	-
4/30/74		6	4.7	6.7									120	120	70	40	150	280	1.0	-		
5/1/74		6	4.7	6.8															1.5	-	3515	-
5/2/74		6	4.8	7.0	68	0.4	8.9	19.2			2565	930							0.7	-	3715	-
5/3/74		6	4.7	6.8													130	110	2.0	-	3865	-
5/6/74		6																	2.0	-		
5/7/74	Started Pre-Chlorination	6																				
5/8/74	Excessive Foam	6	4.8	6.8	70	0.4	8.9	14.5	835	102	2465	780							1.8	-	4150	
5/9/74	Began NaOH for pH Control	6															130	140				
5/10/74		6																	1.0	-	4180	-
5/11/74		6																				
5/12/74		6																				
5/13/74		6	4.7	7.2	72	0.5	8.0	7.2	680	90	2580	895							1.0	-	4320	-
5/15/74		6	4.7	7.0													135	210	1.0	-	3725	-
5/16/74		6	4.9	7.2	80	0.5	9.2	12.0	740	85	2320	970							1.7	-		
5/17/74		6	4.7	7.2															2.1	-	3495	
5/20/74		6	4.7	7.2	74	0.2	2.8	9.6	660	85	2225	685							3.0		3410	
5/21/74		6	4.7	6.9															1.5		2790	
5/22/74		6																	1.5		2940	
5/23/74		5	4.7	7.0	82	0.2	6.6	6.2	720	90	2070	740							1.5			
5/24/74		6																	3.0	3470		
5/28/74		6	4.7	6.8	74	8	5.4	5.0	695	85	2105	655							0.8	3670		
5/29/74	Stop Pre-Chlorination	6																	0.6	3630		
5/30/74		0																				
5/31/74		0																		3040		

TABLE B.

POST-CHLORINATION

Date	Cl_2 Feed (lb/day)	Cl_2 Residual (mg/l)
2/7/74	7	35
2/8/74	0.5	0
2/9/74	1.5	4.4
2/10/74	1	6.6
2/11/74	0.75	2.0
2/12/74	0.75	1.7
2/13/74	0.75	1.1
2/14/74	0.75	0.5
2/15/74	1	3.3
2/18/74	1	2.4
2/19/74	3	11.6
2/20/74	3	13.9
2/21/74	3	11.1
2/22/74	5	22.4
2/25/74	5	24.4
2/26/74	7	33.4
2/27/74	7	35.2
2/28/74	7	32.0
3/1/74	10	47.4
3/4/74	10	35.7

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(Please read Instructions on the reverse before completing)

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7. AUTHOR(S)
John T. White, T. A. Bursztynsky, John D. Crane and Richard H. Jones

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16. ABSTRACT

A completely mixed activated sludge system was designed for a wood preserving plant with an average daily wastewater flow of 27,000 l/day (7,150 gal/day), a BOD concentration of 1,100 mg/l, and a phenol concentration of 120 mg/l. Included in the design were capabilities for pre- and post-chlorination. The activated sludge system alone was capable of removing 90 percent BOD, 75 percent COD, 99 percent phenol, and 76 percent pentachlorophenol. Post chlorination dosages of over 50 mg/l resulted in 50 and 52 percent reductions of phenol and pentachlorophenol, respectively. Laboratory pre-chlorination studies showed removal of phenol and pentachlorophenol at chlorine dosages in excess of 250 mg/l.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Wood preservatives, *Activated sludge, *Oxidation, Phenol, Creosote	*Completely mixed, *Chlorination, pentachlorophenol.	13/B

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